THE CHEMISTRY and TECHNOLOGY OF MIXED PAINTS

Toch

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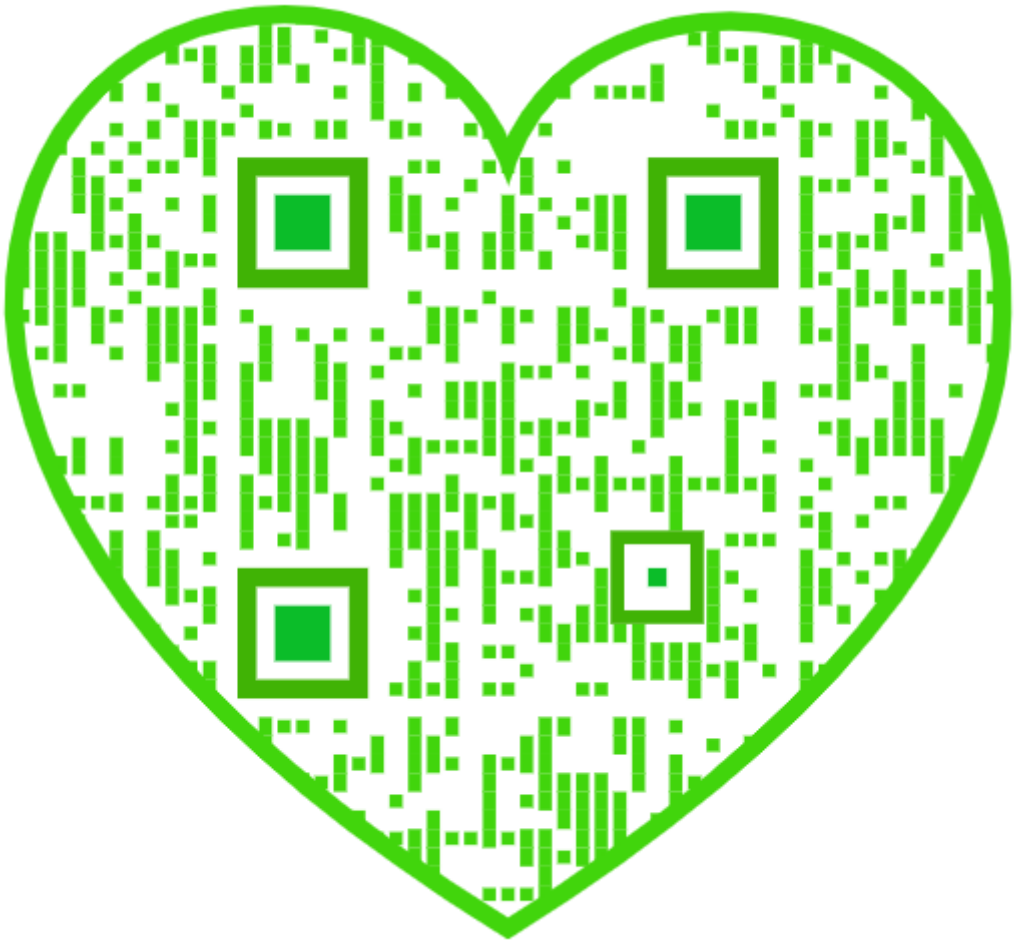

THE CHEMISTRY AND TECHNOLOGY OF MIXED PAINTS

By MAXIMILIAN TOCH
Director of the Laboratory of Toch Brothers, New York City

WITH 60 PHOTOMICROGRAPHIC PLATES AND OTHER ILLUSTRATIONS

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PREFACE

THE difficulty which I encountered in writing this book was not how much to write but how much to omit, for I found on compiling my notes that I could very easily have made two volumes, each larger than the present one, and still I would not have covered the ground thoroughly. It is for this reason that I have omitted many of the pigments which are rarely used, and have paid no attention whatever to the pigments which have gone out of use.

I have not considered it desirable to use any space in this book with extended repetition of matter that can be found in other books of reference, for I have so much matter which is the result of original research that very few references are cited.

This being the first book ever written on the subject of mixed paints, I am cognizant of the fact that there are many matters in it which I shall have to alter in future editions, and many subjects upon which I shall have to enlarge. It must be borne in mind that mixed paint is demanded by a progressive civilization and that there are no two manufacturers who make identically the same mixtures. As time changes, the progressive manufacturer alters his formulas, and an indication of this is that the original mixed paints which were made were mostly emulsions and soap solutions, whereas to-day the tendency is toward purity and improve-

ment and one manufacturer tries to outdo the other in making a paint that will last, the ideal paint, however, being never reached.

This volume is intended for the student in chemistry who desires to familiarize himself with paint, or the engineer who desires a better knowledge of the subject, or for the paint manufacturer and paint chemist as a work of reference. It is not intended for those who have no previous knowledge or training in the subject.

Some of the chapters in this book are taken from my lectures delivered at various universities, and others are extracts from lectures delivered before scientific bodies. One of the objects which I have had in view during the entire time I have been writing this book is to familiarize the student in chemistry, or the post-graduate, with the science and technology of modern paints, so that in a very short time the chemist unfamiliar with the subject may obtain sufficient knowledge to make a reasonable examination of paint.

The chapter on linseed oil illustrates this, and my researches and theories on the difference between raw and boiled linseed oil are here published for the first time. From the formulæ and disquisition on the subject it can be easily seen that if raw linseed oil be taken as a standard nearly all comparisons fail if boiled linseed oil is under examination.

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INTRODUCTION

THE manufacture of mixed paints is essentially American, having been accredited to some enterprising New Englanders who observed that when a linseed oil paint was mixed with a solution of silicate of soda (water glass) an emulsion was formed, and the paint so made showed very little tendency to settle or harden in the package. Several lay claim to this invention. The first mixed paint was marketed in small packages for home consumption and appeared about 1865.

The addition of silicate of soda is still practised by a few manufacturers, but the tendency is to eliminate it as far as possible and to minimize as much as possible the use of an alkaline watery solution to keep the paint in suspension. The general use of zinc oxide has had much to do with the progress of mixed paint, for it is well known that corroded white lead and linseed oil settle quickly in the package, while zinc oxide keeps the heavier lead longer in suspension. Where only heavy materials are used, manufacturers are inclined to add up to 4 per cent of water. Under another chapter on "Water in the Composition of Mixed Paints," p. 117, this subject will be fully discussed.

To the pigments are added many materials possessing

body, hiding or covering property, which are known as inert fillers, and some of these, particularly the silicates of alumina and the silicates of magnesia, the various calcium carbonates, and silica itself, are used to counterbalance the heavy weight or the specific gravity of the metallic pigments; and whereas these inert fillers were formerly regarded as adulterants and cheapening agents, they are now looked upon as necessities, and the general consensus of opinion among practical and many scientific investigators is that a compound paint composed of lead, zinc, and a tinting pigment, to which an inert material has been added, is far more durable than paint made of an undiluted pigment. The consuming public and the painter himself have not been sufficiently educated as yet to understand the merits of these diluents, and the paint manufacturer has been reticent in his statements regarding the use of various fillers.

These facts account to a large degree for the opposition to the use of such materials. When it is taken into consideration that within forty years the sale of mixed paint in the United States has grown to almost sixty million gallons per year, and the outlook is for a larger increase in the use of mixed paints, it is obvious that the demand is healthy, even though the manufacture of mixed paints has been directed or based largely upon empirical formulæ.

One of the railroads of the United States buys at this writing upwards of one million dollars worth of paint material per year, a large share of this being mixed paints, or paint ready for the brush. Nearly all of the large manufacturing industries which use large quantities of paint are gradually altering their methods, so that their paint comes to them ready for application. In no case, to the best knowledge of the author, does a single one of these industries

prescribe a single pigment reduced with linseed oil for general purposes, for it has been shown that a mixture of several pigments and a filler is superior from the standpoint of lasting quality and ease of application to a mixture of a single strong pigment and the vehicle.

The structural iron industry, which has reached an enormous development in the United States, uses paints ready mixed with the one exception of red lead, which, in the old prescription of thirty-three pounds of red lead to one gallon of oil, cannot be prepared ready for the brush, for reasons which will appear in the proper chapter.

The manufacture of agricultural implements, wagons and wire screens can be cited as industries in which manufacturers have within a very few years adopted the use of ready-mixed paints for their products. These paints are not brushed on, but are so scientifically made, and the difference between a vehicle and a pigment is so carefully observed, that large pieces of their products are dipped into troughs and the paint allowed to drain. The surface is more evenly coated and the work done in far less time than would be required were it applied by means of the brush, as in former years.

In view of all these facts, the prejudice on the part of the general public and the trepidation of the manufacturer are to blame for the unheralded knowledge of the constituents of mixed paints. There are many cases where materials which were once despised are regarded now as essential to the life and working quality of paint, and the attitude of the paint manufacturer must in the future be a frank and open admission of the composition of his materials. If a paint is composed of a mixture of white lead, zinc oxide, and barytes, and it has been proved that a mixture of these three will

outlast a mixture of either of the other two, there is no reason why a manufacturer of mixed paints shall not so state.

New materials have come into use which have taken the place in a large degree for many purposes of the time-honored and useful white lead, and many mixed paint manufacturers have already begun to educate the public to the superiority of one material over another. It stands to reason, however, that the manufacturer of a raw material which has been in use for a very long time is going to refute as much as possible the statement made with regard to newer materials, and these discussions tend to do good rather than harm.

In the case of one of the large railroads, the specifications for a certain paint demand the use of over 70 per cent of inert filler, and if these inert fillers had no merit or had a tendency to deteriorate the quality of the paint, no railroad or large corporation would permit their use. These large corporations support chemical laboratories and employ the best talent which they can engage. They continually experiment, and in their specifications the results of their experiments are obvious, and therefore if a large corporation can state publicly not only what the composition of these paints shall be, but conclude that such compositions are based upon the results of scientific investigation, the paint manufacturer can do likewise and stand back of his products provided they be mixtures of various materials which time, science, and investigation have proved to be superior.

Unfortunately, however, there are some manufacturers who have "hidden behind a play of words" and permit chicanery and finesse to enter into the description of their products; but fortunately some of them have seen the errors

of their ways, and already there is a tendency for openness and candor with regard to their wares. There was a time, and it still exists in a measure, when substitutes for white lead were very largely sold, and misleading labels appeared on the packages; for instance, a man would make a mixture of 80 per cent barytes and 20 per cent white lead, and would print on the label — "The lead in this package is guaranteed absolutely pure," followed by a commendation and guarantee that certain sums of money would be paid if the lead were not found to be pure. This, of course, is a moral fraud and an unfortunate play on the ambiguity of the language, and many of the manufacturers, in view of such unfortunate misstatements, are altering the names of their paste products, or lead substitutes, omitting the word "lead" entirely.

Another unfortunate mistake is made when a manufacturer makes a mixed paint and states on the label, "This paint is composed of pure lead, pure zinc, pure linseed oil, pure drier, and nothing else." The analyses of the paint have proved that in addition to the "pure" products mentioned three gallons of water was added to every hundred gallons of paint in order to keep the paint in suspension, and that it had not been strained and therefore contained a large amount of dirt and foreign matter. Ethics would clearly indicate that no manufacturer has a moral right to label his paint as being entirely pure and composed of four materials, when as a matter of fact an excessive quantity of water was added which destroyed in a large degree the value of the other materials. In another chapter the question of the percentage of water which may be contained in any paint will be thoroughly discussed. Three per cent is entirely excessive in an exterior linseed oil paint, and a

manufacturer has no right, either morally or legally, to hide behind a misrepresentation of his paint when the paint is largely adulterated for the purpose of overcoming his ignorance in the manufacture.

CHAPTER I

The Manufacture of Mixed Paints

The modern methods of making mixed paint are divided into two classes, which depend upon the specific gravity and fineness of the raw material.

One of the methods employed is to mix the raw material with sufficient linseed oil to form a very heavy paste, the proper tinting material being added during the process of mixing. This paste is then led down from the floor on which it is made into a stone mill and ground. Even when the mill is water-cooled, the mass frequently revolves at such a speed that the paste paint becomes hot. It is then allowed to run from the mill into a trough called the "cooler," or it is stored in barrels to be thinned at some later time. In case the operation is continuous and the paste is thinned at once, it passes from a stone mill to a mixer below which contains the requisite quantity of thinning material composed of oil and volatile thinner and drier, where it is intimately mixed by means of paddles. It is then compared with the standard for shade, and if the tone should not be identical with the former mixing, either tinting material or pigment is added in sufficient amount to produce the proper shade. From the last mixer, known as the "liquid mixer," the paint is drawn off and filled into packages, the final

operation before allowing it to enter the package being to strain it. This method has been used ever since mixed paints have been made. The majority of white paints, or paints of heavy specific gravity, are made in this manner.

The paints of lower specific gravity, varnish and floor paints, are made differently. This method is really the reverse of the old-fashioned method, in that the liquid and pigment are placed in a mixer on an upper floor in the amounts necessary to produce the correct consistency. The paint is run down in a thin stream to the floor below into a mill known as the "liquid mill." The liquid mills revolve very rapidly, the stones being flat.

According to the best practice of making paste paints a grinding surface is supposed to be conical, although there is much difference of opinion on this subject. When the paint has run through the stones of a liquid mill, it comes out of a spout and is then ready for packing, due precaution being taken, however, to strain it twice, once as it passes down into the liquid mill and again as it passes out of the liquid mill. There is much difference of opinion among paint-making mechanics as to the proper surface which a grinding surface shall present; for instance, the first depression in the stone of a mill is deep, tapering toward the edge, and is known as the "lead." From the end of this "lead" fine lines radiate toward the "periphery" of the stone. These are called the "drifts," and the paints containing silica wear off the surfaces of even the hardest flintstone mills, so that in well-regulated factories a man is always employed sharpening the mills, and by the term "sharpening" is understood cutting out the "drifts" and "leads."

Not so many years ago paint mills were composed of either iron or steel, but in modern paint practice mills of

this character have been abandoned, except for use as filling machines. They grind fairly fine when sharp, but inasmuch as all silicious paint materials are harder than steel or iron they become dull in a very short time. Then again, the attrition grinds off small particles of iron, which affect all delicate tints more or less.

The arrangement of the tanks and mills in the factory is of the greatest importance. Taking up first the second method of mixing paint already described, the liquid and white base are mixed in large, heavy cast-iron mixers, which are located on a platform high enough to discharge into a liquid mill. (See Fig. 1, Heavy Mixers.)

The mixed material is ground through this mill and discharged from it into storage tanks situated conveniently on a platform below the floor on which the mill is located, these storage tanks holding from 1500 to 2000 gallons of the ground product. From the storage tanks a pipe-line with its various branches carries the paint to tinting tanks placed at convenient distances from the storage tanks, the latter being high enough to allow the paint, by gravity, to flow through pipes to the tinting mixers. This pipe-line is made of wrought iron, the usual diameter of which is 4 inches, the joints being all flanged so that the pipes may be easily taken apart and cleaned.

Underneath the storage tanks and close to the outlet is a master valve, so that the product in the tank may be shut off at any time and the flow cut out from the system of pipes. Opposite each tinting tank (these tanks should be in parallel rows and numbered to correspond to the tints that are to be made) a 2-in. branch pipe is connected to the 4-in. main, and each of these branches is furnished with a valve to control the discharge into the thinning mixers. The cast-

iron mixers already mentioned should be so arranged that two mixers work in conjunction with one mill. The mill is

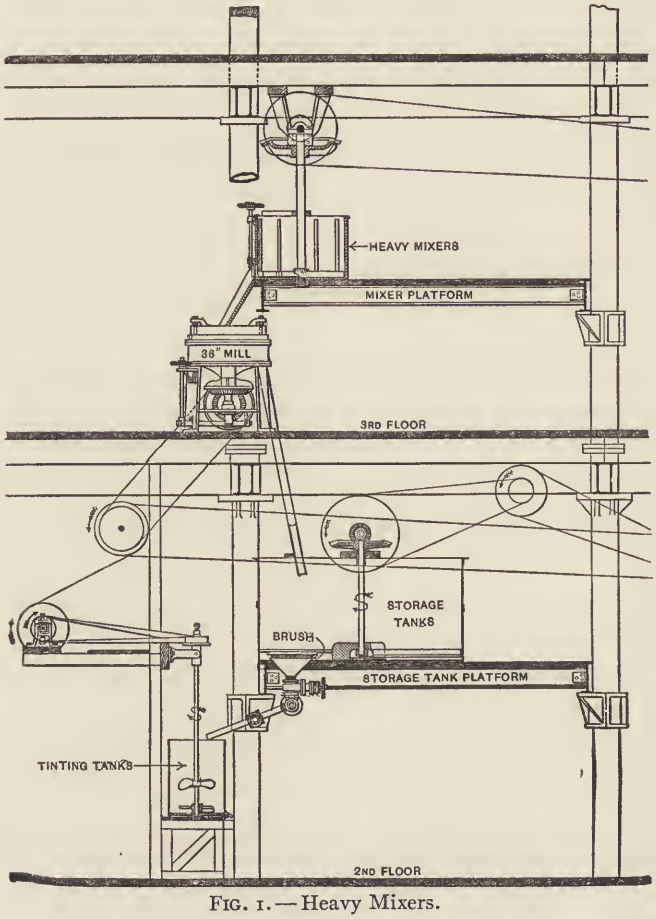
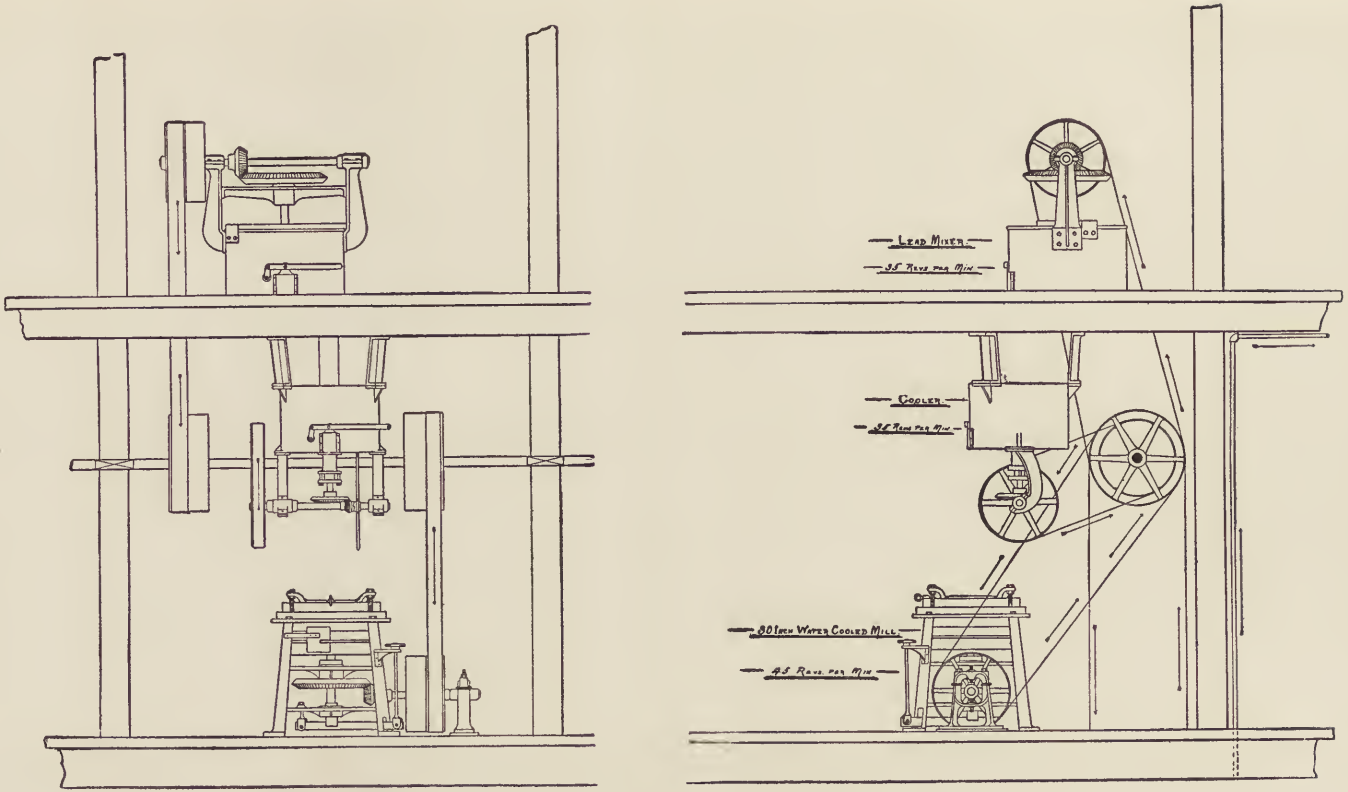


FIG. 1. — Heavy Mixers.

of stone and known as a liquid or encased mill, the usual diameter being 30 to 36 inches.

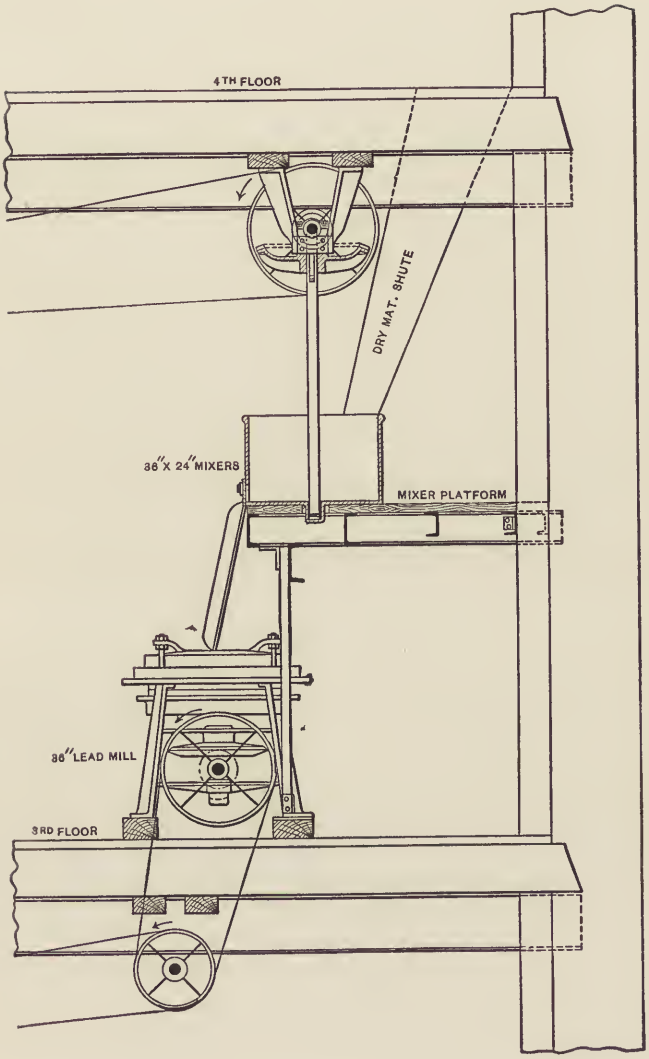
The storage tanks are made of sheet metal with heavy sheet steel bottoms, and are furnished with a slowly revolving stirrer to keep the ground liquid agitated. The outlet of


Lead Mixer
35 Revs per Min
Cooler
30 Revs per Min
30 Inch Water Cooled Mill
45 Revs per Min

these tanks is of generous size and covered with a steel wire screen to prevent any foreign matter such as chips of wood or like material from getting into the supply pipes. Fastened to the stirrer of these tanks is a wire brush which scrapes the surface of the screen in its rotation around the tank, thus keeping the holes of the screen free for the proper flow of the liquid. The tinting colors used in this process are usually ground through small stone mills of 15 in. or 20 in. diameter, and are stored in convenient portable receptacles.

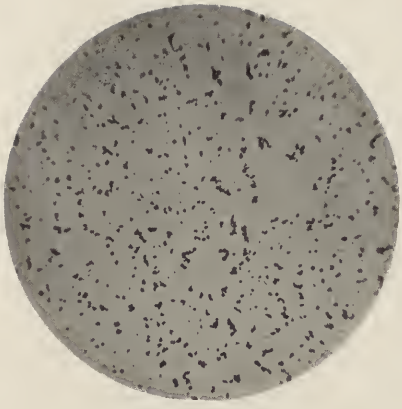
This method of liquid paint-making reduces the handling and labor cost to a minimum, the hardest work being done on the mixer platform where the dry pigment and the proper amount of liquid are first mixed. In a factory where the floors are not arranged so that the method already described can be carried through by gravity alone, it is possible and practicable to introduce a force pump, preferably of the rotary type, to make up for this deficiency. When this latter method is used, the cast-iron mixer and mill should remain in the same relative position as before, but the storage tank could be placed in any other part of a building and on the same floor as the liquid mill, but high enough to discharge by gravity into the tinting mixers. The ground pigment would then be discharged into a small tank situated at the foot of the mill, to which the rotary pump is attached. As this tank is filled with the ground product, the pump would force it through the proper pipe connection to the storage tank, the connection from the storage tanks to the tinting mixers being the same as in the first described process.

The second method in use is to mix and grind the pigment in paste form, using the same style of mixer; but instead of a liquid mill a paste mill is used. Situated at

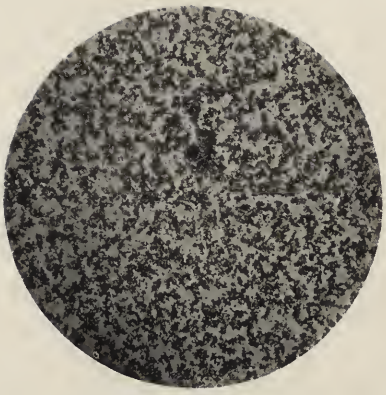

4TH FLOOR
DRY MAT. SHUTE
36"X 24" MIXERS
MIXER PLATFORM
36" LEAD MILL
3RD FLOOR

the back of this paste mill, and close to the discharge scraper, is a steel tank of generous dimensions (usually 500 gallons), into which the ground pigment is discharged. This steel tank is provided with a stirrer for mixing the ground pigment with the oil and other thinners that are added to it, in order to reduce it to a liquid form. It is then carried to the tinting tanks by a pipe-line on the same general plan as that heretofore described.

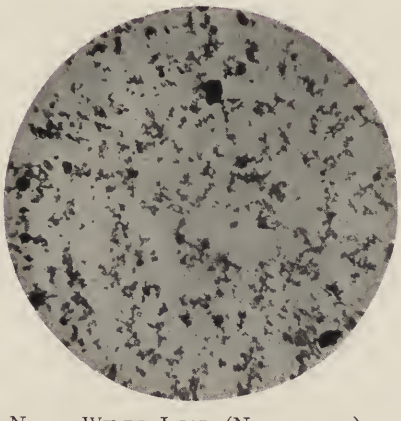
One of the advantages of this plan is that this outfit can be used in a dual capacity, *i.e.*, it can be used for the mixing of liquid paints after the plan described and, by changing the scraper from the back to the front of the mill, the outfit can be changed into a paste-grinding plant.



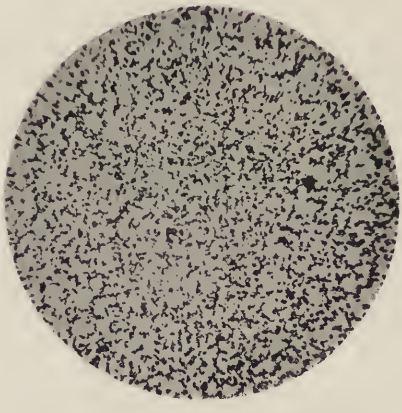
No 1. Sublimed White Lead — Photomicrograph X250, showing great uniformity of grain.



No. 2. Corroded White Lead — Photomicrograph X250, of known purity and composition.



No. 3. White Lead (New process) — Photomicrograph X250.



No. 4. Standard Zinc Lead White — Photomicrograph X250.

THE PIGMENTS

CHAPTER II

White Pigments

The white opaque pigments used in making mixed paints are white lead, zinc oxide, sublimed white lead, standard zinc lead, lithopone and sulphopone.

Among the white leads there are several varieties; the principal ones, however, are the old Dutch process lead and the quick process lead, both of which are hydrated carbonates of lead.

There are many varieties of zinc oxide made in the United States, depending largely upon the raw material. The grade made principally from spelter, according to the French process, is known in America as "Florence Red and Green Seal Zinc." The seals on zinc indicate the whiteness of color, the green seal being the whiter. In Germany the colored seals extend to a greater range than in America, the green seal being the whitest, the red next, the blue next, the yellow next, and then the white.

The New Jersey zinc oxides are made direct from the ore and are almost as pure as the zincs made from the metal, but they have a totally different tone, being much more of a cream color than the so-called French zincs.

The Mineral Point zincs made in Wisconsin contain a varying percentage of sulphate of lead. The leaded zincs of Missouri are in composition analogous to those of Mineral Point, but the percentage of sulphate of lead is much higher.

The standard zinc lead white of Colorado contains 50 per cent oxide of zinc and 50 per cent sulphate of lead. Sublimed white lead is made in Joplin, Missouri, from Galena mineral, and will average 95 per cent oxysulphate of lead and 5 per cent zinc oxide.

Lithopone is a double precipitate of sulphide of zinc and sulphate of barium. Sulphopone is a new white paint which has not been produced in America in commercial quantities, but is similar in composition to lithopone, with the exception that the sulphate of barium is replaced with sulphate of calcium.

These are the opaque white pigments used in the manufacture of mixed paints. It is not within the power of any man to say which one of these is the best, because under certain circumstances one material will outrank another and long practice has demonstrated that no single white pigment material is as good as a mixture of various white pigments for mixed paint. The differences of opinion and conflicting reports that one hears concerning these raw materials is largely due to competition among manufacturers. Whenever a new material is exploited a manufacturer of a tried and staple pigment naturally finds the defects in the new material and informs his salesmen to this effect. And so when a material finally succeeds and takes its place among the recognized list of pigments it has gone through all the hardships and vicissitudes possible.

For two thousand years, more or less, there was no other white pigment than white lead. Within the lifetime

and memory of many a paint manufacturer in the United States, all the pigments described in the beginning of this chapter have been born and have prospered. The great competitor of white lead is zinc oxide, and the weakness of white lead is the strength of zinc oxide, and vice versa. White lead, for instance, is a soft drier and zinc oxide is a hard drier. White lead finally becomes powdery; zinc oxide in its eventful drying becomes hard, and it is for these reasons that a mixture of zinc oxide and white lead forms such a good combination. On the other hand, it is regarded as a fact that a paint composed of an opaque white pigment in a pure or undiluted state should not be used, for experience and chemistry have both shown that an inert extender added in moderate proportions to the solid white pigment increases its wearing power, and when the final surface needs repainting it presents a better foundation for future work. Taking all of these facts into consideration, a paint manufacturer who combines experience with the teaching of chemistry is quite likely to produce a material that will add both to his reputation and his income. He certainly has a great advantage over the man who works entirely by rule of thumb.

A manufacturer who in making mixed paints puts into his material 90 cents' worth of pigment and oil cannot hope to succeed if he sells his paint in gallon cans at $1.20, for the reason that a margin of profit of 30 cents is insufficient on account of the high cost of selling. Out of this 30 cents profit, the gallon can together with the label and cost of closing is 10 cents. This leaves 20 cents. The advertising and color card schemes which are distributed are estimated at from four to five cents per gallon. This leaves a trifle over 15 cents per gallon. The salesmen's commissions, salary, and traveling expenses are estimated at 6 cents per

gallon, and the cost of making the paint, paying freight, and interest on the investment due to abnormal credits, are generally estimated at 10 cents per gallon. Consequently the cost of the paint on delivery to a customer is equal to $1.20 per gallon, if the raw material should cost 90 cents. The manufacturer is, therefore, a credit to the community if he reduces the cost of the raw material in his paint to 70 cents per gallon, provided he does not give them an inferior article, but it will be shown in the following pages that the proper pigment mixed with the proper extenders or fillers produces not only a good paint but in many instances a far better paint than is produced by the use of a mixture of solid pigments alone. No merchant or manufacturer is a credit to the community if his business is a losing one, for he creates hardships among his employees, and if his business be unprofitable he cannot pay his workmen as much as they deserve.

White Lead

Formula, $2PbOCO_2$, PbH_2O_2; Specific Gravity, 6.323, 2, 6.492.

White lead is the oldest of all white paints, and prior to the middle of the last century it was the only white pigment in use with the exception of a little zinc and bismuth. Within half a century quite a number of other white pigments have come into use, and only gradually have the defects of white lead become known. The history of this pigment, its method of manufacture, and the general uses to which it has been applied, are so well known and are generally given even in elementary text-books on chemistry that it is not the author's purpose to take up much space for this subject.

Briefly stated, however, there are two processes for the manufacture of white lead; one called the Dutch process, which takes about ninety days and is a slow corrosion of a buckle of lead in an earthenware pot in the presence of acetic acid. Carbonic acid from fermenting tan bark acts on the lead, converting the material into hydrated carbonate of lead. In the other, which is called the quick process, the acetic acid solution of lead is directly acted upon by either carbonic acid gas or an alkaline carbonate salt. The old Dutch process is still much more largely used than the quick process, the resulting product being much more desirable from the practical standpoint. There are a number of other processes under a variety of names, but none of them differ very much from the so-called "quick process."

White lead is in great favor with the practical painter, not for its wearing quality but principally for the freedom with which it is applied. Although white lead is generally spoken of as a carbonate of lead, it is composed of approximately 69 per cent carbonate of lead, $PbOCO_2$ and 31 per cent of lead hydroxide PbH_2O_2. It is this lead hydroxide which combines quite rapidly with oil and forms an unctuous substance sometimes known as "lead soap." White lead is variable in composition, the amount of hydrate ranging from 15 to 30 per cent. In addition to this, during the process of manufacture of the old process lead, and after its final washing, it is mixed with linseed oil while still in the wet state. The oil having a greater affinity for the white lead than the water has, the latter is displaced. A small percentage of moisture adds to the free working quality of the paint made from white lead. (See "Detection of Water in Paints," page 119.)

White lead is regarded as a poisonous pigment, and so

it is, but this property should not condemn it for application to the walls of a house or for general paint purposes, because its toxic effect cannot be produced from a painted surface. Its poisonous quality is manifest to the workmen in the factories where white lead is made, and also to the painter who is careless in applying it. The unbroken skin does not absorb lead very rapidly, but the workmen inhaling lead dust, or the painter who allows a lead paint to accumulate under his finger nails, is likely to suffer from lead poisoning. In one or two factories where much white lead is ground, a small percentage of potassium iodide is placed in the drinking water. This overcomes any tendency toward lead poisoning, by reason of the fact that the soluble iodide of lead is formed in the system and the lead is thus flushed out through the kidneys. Charles Dickens, in one of his short stories called "A Bright Star in the East," comments on the misery produced in a certain white lead factory in London, and expressed the hope that American ingenuity would overcome the dangers which beset the men. In one of the largest white lead works in New York City lead poisoning does not occur, owing to the ingenuity and care exercised by the management.

The ratio of oil necessary to reduce white lead to the consistency of paint can by no means be given in exact figures. The old Dutch process lead will take four and a half gallons of linseed oil to one hundred pounds of white lead ground in oil, in order to obtain a paint of maximum covering property. The new process lead will take more oil than this, and in many instances up to six gallons to the one hundred pounds of white lead paste, which contains approximately $1\frac{1}{10}$ gallons of linseed oil. On a mixed paint basis, 60 pounds of dry white lead will take 40 pounds of

linseed oil to produce the correct ratio, but in addition four pounds of volatile thinner, such as benzine or turpentine, can be added to increase the fluidity and assist in the obliteration of brush marks. No general rule can be given for the percentage of oil necessary, as temperature has much to do with this, but the difference in the amount of oil necessary to produce a good flowing paint during summer or winter can be approximately given as 10 per cent, less vehicle being necessary in summer than in winter.

White lead when exposed to the elements becomes chalky after a while and assumes a perfectly flat appearance which resembles whitewash, and comes off very readily on the hand. As long as there was no remedy for this there was no comment on the subject, but at the present time investigators have improved paint mixtures so that this defect is not so palpable as it was in former years. From many experiments made by the author the causes of the chalking of white lead may be summarized as follows:

First. The action of the carbonic acid in rain water.

Second. The action of sodium chloride (salt in the air).

Third. The catalytic action of white lead itself in being a progressive oxidizer of linseed oil.

First. If white lead be treated with water containing carbonic acid it is found that the same solvent action takes place upon carbonate of lead as takes place upon calcium carbonate.

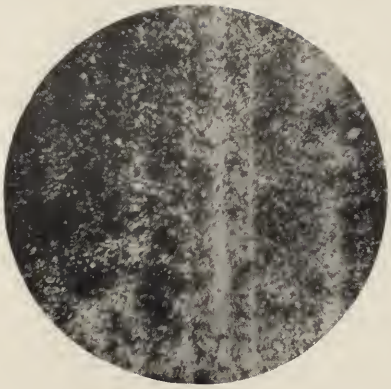
Second. If white lead be treated with a sodium or ammonium chloride solution a solvent action is apparent, and as sodium chloride is always present in the air at the seashore, and carbonic acid is everywhere present in the atmosphere and is readily taken up in a rain storm, the chalking of white lead can be attributed to these causes.

The *third* cause is, however, problematical and cannot at this writing be stated with any degree of positiveness. It is quite true that white lead and linseed oil do not attack each other so readily on an interior wall as they do on a wall exposed to the elements.

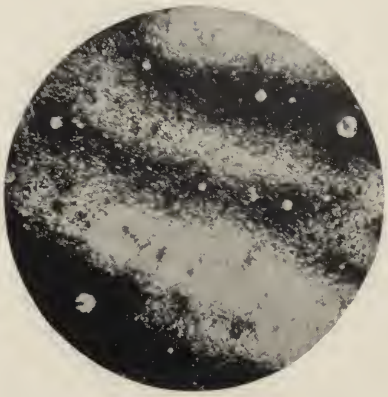
One of the defects mentioned by many writers on white lead is its susceptibility to sulphur gases. In nature these sulphur gases are generated in two places; namely, in the kitchen of every house, and in and around stables and out-houses. In kitchens, the cooking of vegetables liberates hydrogen sulphide to a great extent, the odor of which is familiar to everybody who comes into a house where either cauliflower or cabbage is being cooked. But, inasmuch as undiluted white lead is not often used for interior painting, the defect is not so noticeable. A few stables or out-houses are painted pure white, and when they are painted white the painter generally has sufficient knowledge of the subject to use zinc oxide instead of white lead.

It cannot be denied that the ease of application of white lead, as well as its enormous covering property, has had much to do with the preference for it as a paint. With the exception of lithopone, it has a greater hiding property, volumetrically considered, than any other white paint; on the other hand, gravimetrically considered, it has less body than any of the lighter paints.

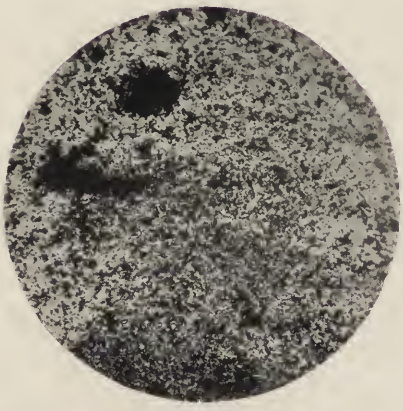
The addition of an inert filler, such as artificial barium sulphate, silica, and barytes, improves white lead considerably. These inert fillers, which will be considered under their proper chapters, are not affected by chemical influences in the slightest degree, and where they are used in the proper proportions, additional wearing quality or life, as the painter calls it, is given to the paint. The percentage



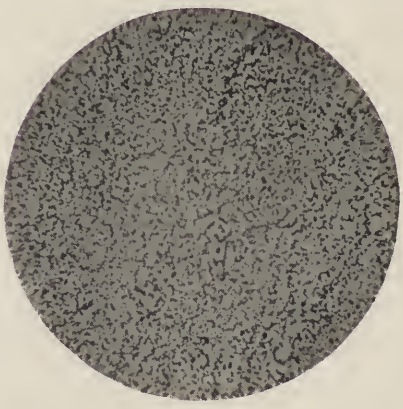
No. 5. Red Lead — Photomicrograph X200 of paint film freshly applied, showing separation of the pigment from the oil.



No. 6. Red Lead — Photomicrograph X150, applied one hour after mixing, showing separation and air bells encysted in film.



No. 7. French Orange Mineral — Photomicrograph X250, not very uniform in grain.



No. 8. American Zinc Oxid — Photomicrograph X300, very pure and very uniform in grain; this oxid is made direct from the ore.

of inert fillers which can be added to white lead varies up to 50 per cent. More artificial barium sulphate than natural barium sulphate can be added. If a comparative exposure test be made, both on wood and metal, of undiluted white lead and white lead containing an inert extender, it will be found that at the end of eighteen months the paint which contained the filler is in a better state of preservation than that which did not contain it. Generally considered, white lead is an excellent paint, more particularly when added to other materials.

Sulphate of Lead

Formula $PbSO_4$

It must be borne in mind that the sulphate of lead of commerce, which is not so frequently met with nowadays as formerly, is a very poor paint material, and it must not by any means be confounded with sublimed white lead which is, at times, erroneously called lead sulphate.

The lead sulphate of the paint trade is a nondescript article which was sold as a by-product by the textile printers who used acetate of lead as a mordant, and to this liquid sulphuric acid was added and the precipitate was sold to the paint trade under the name of lead bottoms or bottom salts. Occasionally this material is still met with, and wherever it is used in a mixed paint it does more harm than good. It is likely that the pure neutral lead sulphate, which is a good oxidizing agent, dries well and covers fairly well, could be used for ordinary light tints if diluted with the proper inert materials, but the lead sulphate which is sold by the textile printers is always acid and is sometimes coarse and crystalline, and at other times quite fine.

The chemist, the paint maker, and the engineer must never confound this lead sulphate with the lead sulphate contained in sublimed lead, zinc lead, or leaded zincs.

Sublimed White Lead

Specific Gravity, 6.2.

Sublimed white lead is an amorphous white pigment possessing excellent covering and hiding power, and is very uniform and fine in grain. It is a direct furnace product obtained by the sublimation of Galena, and within the last ten years it has come into great prominence among paint makers, it now being regarded as a stable, uniform, and very valuable paint pigment. The author has examined a great many paints containing sublimed lead. Among one hundred reputable paint manufacturers in the United States sixty-five used sublimed lead. About eight thousand tons were used in the United States in 1905. Considering the fact that sublimed lead as a pigment is about twenty-five years old, it is very likely, judging from its qualities, that it will be used more universally and in larger quantities in the future.

When mixed with other pigments, such as zinc oxide, carbonate of lead, and the proper reducing materials added, such as silica, clay, barium sulphate, etc., it produces a most excellent paint, and at the seashore its wearing quality is superior to that of carbonate of lead. In composition it is fairly uniform. From the analysis of thirty-four samples of sublimed lead its composition may be quoted as 75 per cent lead sulphate, 20 per cent lead oxide, and 5 per cent zinc oxide, although each of these figures will vary slightly either way. Corroded white lead also varies in its percent-

age of hydrate, but for analytical purposes a constant must be admitted which will fairly represent the composition.

The question has arisen of late years whether sublimed lead is a mixture of the three components just cited, or whether it is a combination of lead sulphate and lead oxide with the mechanical addition of zinc oxide. Inasmuch as all the lead oxides that are known in commerce or in chemistry are yellow, red, or brown, it is held by many that the lead oxide of sublimed lead is really an oxysulphate, or, in other words, a basic sulphate of lead. A mixture of precipitated lead sulphate, litharge, and zinc white in approximately the proportions found in sublimed lead, when ground in oil and reduced to the proper consistency, dries totally different from sublimed white lead; in fact, sublimed lead when ground in raw linseed oil takes two days to dry dust free, but the mixture just cited will dry sufficiently hard for repainting in twelve hours, because lead sulphate is a fair drier and lead oxide a powerful one. Yet the oxysulphate, having the same composition, behaves totally different from the mixture and in addition is of a different color.

Under the microscope, sublimed lead shows the absence of crystals and remarkable uniformity of grain. Being a much more complete chemical body than the other lead paints, it does not react on linseed oil and therefore makes a much more durable paint compound. It has been urged that sublimed lead is not as susceptible to sulphur gases as white lead, but this the author has not been able to substantiate, for while it may take hydrogen sulphide a longer time to discolor it, it is simply a question of degree and it is acted upon by sulphur gases, although not as quickly as white lead.

Sublimed lead can be determined in a white mixed paint

without any difficulty, owing to the established ratio between lead oxide and lead sulphate. The percentage of free zinc sulphate in sublimed white lead varies from a trace to a half per cent, and many times a chemist will report more zinc sulphate than is actually present, because in washing or boiling a dry or extracted sample the lead sulphate may interact with the zinc oxide and show a larger percentage of zinc sulphate than is really present in the dry products before analysis.

Sublimed white lead as a marine or ship paint is of much value, owing to its hardness of drying and imperviousness of film.

Standard Zinc Lead White

The ores utilized in the manufacture of this material are what are known in mining parlance as "Low Grade Complex Ore," originating in and about Leadville, Colorado; Low Grade, inasmuch as the gold, silver, and copper contents are in quantity too small to warrant the excessive cost of refining. Naturally this ore contains varying percentages of zinc blende or sphalerite and Galena or native lead sulphide, and in order to furnish the product with the proper proportions of lead and zinc, the ores are first analyzed, mixed in their proper proportions and volatilized at a heat of from 2200 to 2500° F. In the volatile state it is carried to the combustion chamber, where the chemical transformation of the product, due to oxidation, completes itself. The white fume is collected in woolen bags, further oxidized on open hearth furnaces, whitened, and then bolted.

The pigment carries approximately 50 per cent pure zinc oxide and 50 per cent lead sulphate, which have com-

bined at an intense heat in vapor form, the union being far more intimate than anything that could be obtained by mechanical means.

This pigment was first put upon the market sixteen years ago and has been popular in the mixed paint trade for a period not exceeding ten years, and within the last five years it has become more uniform and is regarded as a valuable paint material by a great many mixed paint manufacturers.

The percentage of zinc sulphate will vary, but under normal conditions it will seldom go higher than half of 1 per cent.

The color, while it is not as white as zinc oxide, is about the same shade as the average corroded white lead. The pigment can be used to great advantage in combination leads, graded leads, primers, floor paints, and ready mixed paints. Its specific gravity is approximately 5.5 and its composition theoretically 50 per cent pure zinc oxide and 50 per cent lead sulphate. The pigment generally contains a trace of silica, iron, and alumina. A very small portion of the lead is in the form of a basic lead sulphate, and the pigment undoubtedly takes up a little moisture on standing. Its average analysis shows the following composition:

$PbSO_4$ ..... 50.00 per cent.
ZnO ..... 49.55 per cent.
$ZnSO_4$ ..... .40 per cent.

The percentage of zinc sulphate will vary slightly, but under normal conditions it will seldom average higher than $\frac{1}{2}$ of 1 per cent, and where it does average more than this it is frequently due to the fact of long continued boiling in the flask, which causes a reaction between lead sulphate and zinc oxide.

Analyses of Standard Zinc Lead White

$PbSO_4$	48.90	50.00	49.22	49.80	50.15	48.87
ZnO	50.50	49.55	50.41	49.90	49.25	50.82
$ZnSO_4$	.25	.40	Trace	.20	.12	Trace

Photomicrographs of zinc lead show a uniformity of grain, and microscopic investigations fail to show anything but a homogeneous product. It is very stable; when exposed to the air mixed with a proper proportion of linseed oil and drier, as compared with a mixture of 50 per cent corroded white lead and 50 per cent zinc oxide, it will be seen that the film of paint composed of zinc lead is superior to that of corroded white lead, for it retains its gloss longer and does not show as much indication of chalk as the other mixture. Like white lead, it whitens on exposure, but holds up in suspension better, as indicated by its low specific gravity. When a paint is made on a zinc lead base ground in pure linseed oil, it will not separate, form a cake, or make a sediment; neither will it peel, chalk off, or turn yellow.

Zinc Oxide

Formula, ZnO; Specific Gravity, 5.2.

Zinc oxide as a paint pigment is only fifty years old, and when it is taken into consideration that in that short space of time its use has grown until in 1905 nearly seventy thousand tons were used in the paint industry in the United States, it speaks for itself that the material must be of exceptional merit to have advanced so rapidly. At the same time, although it is impossible to obtain any exact figures on the subject, it is probable that more than one half of this seventy thousand tons were used in connection with other materials.

The discovery of zinc oxide by Le Clair in France and Samuel T. Jones in America are sufficiently well known, and have been quite thoroughly written up in other books. The former made zinc oxide by subliming the metal; the latter made it by subliming Zincite and Franklinite ores. The specific gravity of zinc oxide will average 5.2, and fifty pounds will take fifty pounds of linseed oil; in other words, to produce the proper mixed paint it will require a far greater proportion of linseed oil than white lead will take. It is generally stated in text-books that zinc oxide is not affected by sulphur gases and therefore will not turn color. This statement is not exactly correct, the author having always contended that zinc oxide is not *visibly* affected by sulphur gases, but there is no doubt, as any chemist will admit, that zinc oxide is affected by sulphur gases, although not to the same extent as white lead. As zinc sulphide, zinc sulphite, and zinc sulphate are white products, the absorption is not evident to the eye, and hence the erroneous statement has crept into use that zinc oxide is not affected by sulphur gases.

When mixed with linseed oil and the proper amount of drier it sets and dries much more slowly than white lead. Nevertheless this drying continues in the form of progressive oxidation until the surface becomes very hard. A comparison between zinc oxide and white lead paints will show that the progressive oxidation which takes place when white lead dries, produces a chalky mixture, while the reverse is true of zinc oxide, which will produce a hard and brittle vitreous surface which is somewhat affected by temperature changes. Owing, therefore, to the diverse effects of the two pigments, a combination of lead and zinc is often well recommended. The hard drying zinc has not, however,

been very well understood. Fifteen years ago the author undertook a series of experiments and found that the drier was very largely responsible for the hardening action of zinc. If the linseed oil be prepared with litharge (PbO), the resulting zinc paint will last far longer and be much more flexible and consequently not readily cracked when exposed to a variation of temperature of even 130°, such as we have in this climate. If, however, a drier is used in which manganese (MnO_2) and red lead (Pb_3O_4) have been cooked with the oil, the action of the manganese continues until a vitreous surface is the result. It is owing to the result of these investigations that the use of American zinc oxide made from Franklinite ore has become so general for the manufacture of white table oilcloths. (See Journal of Society of Chemical Industry, No. 2, Vol. XXI, Jan. 31, 1902.)

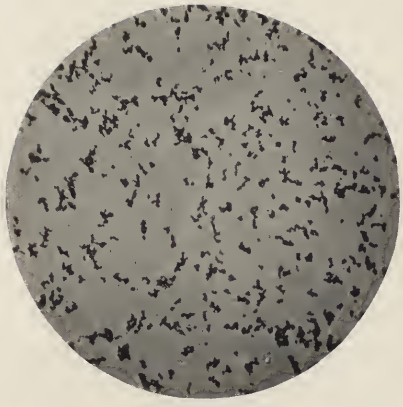
When enamel paints are made of an oil varnish and zinc oxide, and the drier in the varnish is composed of manganese and lead, the enamels eventually become hard, evidently through the catalytic action of the manganese. It is desirable to omit the manganese in high-grade enamels, or, where manganese must be used, in order to obtain a rapid setting the borate of manganese should be employed, but only in very small quantities.

The American zincs are:

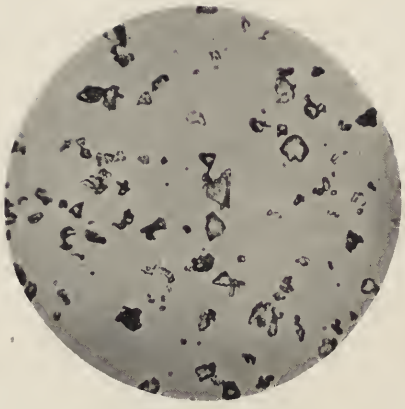
First. The Florence Red and Green Seal zincs, which are made by the sublimation of the metal and are practically pure and equal in all respects to those made in France and Belgium.

Second. The New Jersey zinc oxides, which are made from Franklinite ore and are free from lead and frequently run over 99 per cent ZnO.

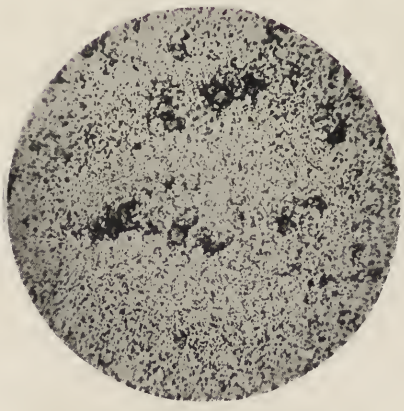
Third. Mineral Point Zinc, which is made at Mineral



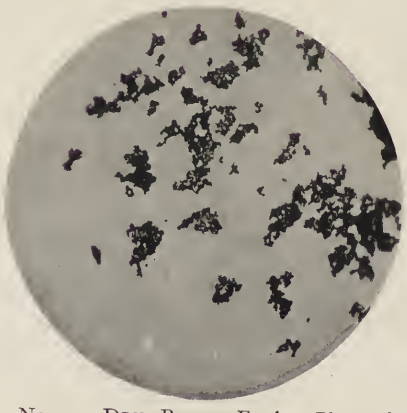
No. 9. FRENCH GREEN SEAL OXID—Photomicrograph X300, much whiter than the American Zinc made from the metal, but coarser in grain.



No. 10. SILICA—Photomicrograph X250, finely powdered and air floated, uniform angular grain.



No. 11. GERMAN BARYTES — Photomicrograph X300, showing two sizes of grain.



No. 12. DRY BLANC FIXÉ — Photomicrograph X300, coarse and crystalline, precipitated from hot acid solutions.

Point, Wisconsin, and contains from 2 to 4 per cent of lead sulphate.

Fourth. The leaded zincs made in Missouri which contain from 4 to 10 per cent of sulphate of lead.

Zinc oxide chalks to some extent in the same manner as white lead, but only if the atmosphere is charged with carbon dioxid or salt. The same experiment which was carried out with white lead in order to show its solubility in a solution of carbon dioxid was carried out with zinc oxide and the same result obtained. Much weight cannot be given to these experiments, because these chemicals are not always present in the atmosphere. They are merely chemical results which demonstrate both the cause and effect, but it is of some interest to know why the paint films perish. The zinc oxides made from western ores are slightly more permanent than those made from the New Jersey ores, and as paint materials they possess the advantage of containing a larger quantity of lead sulphate.

Nearly all zincs contain a small percentage of zinc sulphate. Much unnecessary trouble has been caused by the criticism against zinc sulphate. Where a paint contains moisture or where water is added in a very small amount to a heavy paint in order to prevent it from settling, and not more than one per cent of actual water is contained in the paint, zinc sulphate forms an excellent drier, particularly where it is desirable to make shades which contain lampblack. The outcry against zinc sulphate is unwarranted because as much as 5 per cent is used in making a patent drier. The amount of zinc sulphate, however, in most of the dry zinc pigments probably decreases with age. Zinc oxide or other zinc paint which will assay 1 per cent of zinc sulphate will, when kept in storage for six months,

show decrease in the zinc sulphate to one half of 1 per cent.

In the enamel paints, the presence of zinc sulphate is not a detriment, and in floor paints it might be considered as a slight advantage, for it aids in the drying and hardening. However, too much of the soluble salt is never to be recommended.

Lithopone

Synonym: Oleum White, Beckton White, Charlton White, Ponolith, Jersey Lily White, Orr's White.
Chemical Formula, $ZnO + BaSO_4$; Specific Gravity, 4.2.

When solutions of zinc sulphate and barium sulphide are mixed together in molecular proportions, a heavy flocculent precipitate is formed according to the following reaction: $ZnSO_4 + Aq + BaS + Aq = ZnS + BaSO_4 + H_2O$. The theoretical percentage will be $29\frac{1}{2}$ per cent zinc sulphide and $70\frac{1}{2}$ per cent barium sulphate. This precipitate as such has no body or covering power, and when washed and dried is totally unfit for paint purposes, but John B. Orr, of England, in 1880 discovered that when it is heated to dull redness, suddenly plunged into water, ground in its pulp state, thoroughly washed and dried, its characteristics are totally changed, and it makes a very effective and durable pigment for paint purposes. In the first place, it is then a brilliant white; in the second place, it is extremely fine in texture, and in the third place, it has the same tinctorial strength but more hiding power than pure zinc oxide. Inasmuch as it is a complete chemical compound, it is stable in every medium known for paint purposes, excepting those which are highly acid. It took several years to perfect the manufacture of lithopone, but it may be easily said that

at the present time lithopone is made with great uniformity and has valuable properties, as will hereinafter be shown.

The method of manufacture is quite simple, success depending very largely on the purity of certain materials. It is worthy of mention, however, that the average chemist unfamiliar with both the theory and practice of its manufacture cannot make it successfully. In the first place, solutions of barium sulphide and zinc sulphate of known composition must be made. The fact that they are impure has no effect on the ultimate product, provided the chemist knows the impurities he has to deal with and the simple methods for their elimination. For instance, the zinc sulphate must be free from iron or a yellowish product is the result. The solutions must be standardized for each batch. The impurities can be eliminated during the process of manufacture, or more properly speaking, before they are pumped into the precipitation tub.

The barium sulphide, however, is quite pure, for the reason that metals like copper, iron and manganese, which are likely to be present, form insoluble sulphides. Barium sulphide is made by heating barytes ($BaSO_4$) to dull redness with coal, petroleum residuum, pitch, sawdust, or other materials having a high percentage of carbon. The resulting reaction may be represented by the following equation: $BaSO_4 + 2C = BaS + 2CO_2$, although under many circumstances the reaction is slightly more complicated. After the reaction is completed and before the air can have any influence on the sulphide, the mass is digested in vats and filtered; when the solution reaches a density of 17° Beaumé, long yellowish needle-shaped crystals separate from the mother liquor. These crystals are almost chemically pure barium sulphide.

With the proper concentration of the solutions, proper temperature and speed at which the two solutions are poured together, the resulting precipitate will be of such physical characteristics that it can be most easily filtered and dried. It is then placed in muffles and heated above 920° Fahrenheit, suddenly plunged into water, again ground, washed and dried. It is then ready for the market. The overheating of the precipitate decomposes some of the zinc sulphide and converts it into zinc oxide. All of the earlier manufacturers overheated their product and that is the reason why lithopone formerly contained from 5 to 10 per cent zinc oxide, whereas theoretically it should have contained none. The manufacturers of the present day, however, have overcome all these difficulties, so that a remarkably uniform product is obtained, the percentage of zinc oxide being small indeed.

We have here an excellent example, as has been stated under another chapter, of a pigment containing 70 per cent barium sulphate, which may be regarded as perfectly pure and normal, and yet twenty-five years ago any pigment containing far less barium sulphate than lithopone would have been regarded as adulterated. No man can reasonably state that barium sulphate is an adulterant to lithopone, for the obvious reason that it is a constituent part of the pigment.

Lithopone has gone through many vicissitudes; no pigment has been blackguarded quite as much as this, and yet no pigment has survived its condemnation as well as this. Almost every paint manufacturer in the United States finds some excellent use for it. It has, however, one characteristic which cannot be explained at present, and this is its power to absorb light and give it out again. This occult, power of zinc sulphide is called the photogenic quality.

Under normal circumstances, if lithopone be mixed with any vehicle containing linseed oil or varnish and exposed to the sunlight, it turns gray very readily, and if again placed in the dark it returns to its normal white color. (See "Toch," on the Composition of Paints and Raw Materials, J. S. C. I., Vol. XXI.) The author is pleased to announce that during a conversation held with Professor William Ostwald, of Leipsic, Professor Ostwald stated that he was applying for two patents on processes which would eliminate the photogenic qualities of lithopone.

It has always been assumed by chemists that this discoloration of lithopone was due to its reaction with lead, and that a lead sulphide was formed which accounted for the color; but investigations have shown that this is not true, for in the manufacture of floor oilcloth, where lithopone is so very largely used, a lead drier is always used and no gray color results. If the chemical properties of zinc sulphide are looked into it will be found that it is abnormal for zinc sulphide to liberate its sulphur in the presence of any neutral salt; even in the presence of organic acids, zinc sulphide is perfectly stable, showing how strong is the chemical union. It has further been claimed that if lithopone does not turn gray it will turn yellow when used as an interior paint, but inasmuch as this is true of any white pigment containing a soluble salt, the fault cannot be imputed to the lithopone, but rather to its manufacture.

Lithopone is likewise very largely used in the cheaper grades of enamel paints, because it does not combine with rosin or semi-fossil resin varnishes and therefore remains unaltered in the package. But, inasmuch as this book does not treat of enamel paints which are, strictly speaking, varnish paints and cannot be classed as ready-mixed oil paints,

a disquisition on the subject must be left to another occasion. As an interior white, a first coat white, a ready-mixed flat paint for surface, or as a pigment in the lighter shades for floor paints, lithopone cannot be excelled for its body, durability, hardness, fineness of grain, and ease of application. It does not oxidize progressively and this single feature has made it invaluable to the table oilcloth and floor oilcloth industry throughout the world. Its indiscriminate use, however, is not to be recommended, and the paint chemist should be permitted to decide when its value is the greatest. As a marine paint, either as a first coat or for making neutral paints where other whites would be necessary, it is found to outlast both zinc oxide and lead carbonate.

CHAPTER III

The Oxides of Lead

The oxides of lead used in making mixed paints are principally litharge, which is PbO, and red lead or orange mineral, Pb_3O_4.

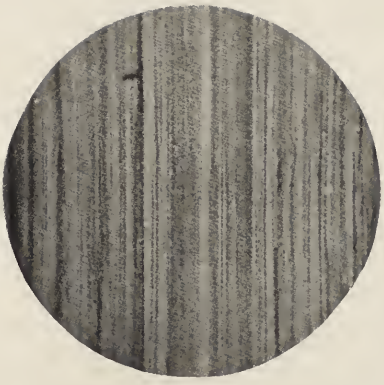
Litharge is made by heating metallic lead to a given temperature in the presence of air, a yellowish ochry powder being formed which has always been regarded as the proper material for manufacturing flexible drying oils. In the chapter on *Linseed Oil* the use of litharge is discussed. It is not generally known that litharge is quite largely used in mixed paints, and all the statements that litharge is useless as a pigment, and has no value as a paint, are misleading, for under certain conditions litharge is indeed a very valuable pigment. It is quite true that a mixed paint containing litharge is unstable and very prone, particularly in the presence of moisture, to form a lead soap and gelatinize the paint. This gelatinous looking compound is what is known among paint manufacturers as "livering," although the "livering" of paint may be due to many causes other than this. On the other hand, a number of black paints which are composed of lampblack, carbon black, charcoal, or a mixture of these, are held together by the use of litharge,

and where these paints are used within a month or two after they are made they serve their purpose most perfectly.

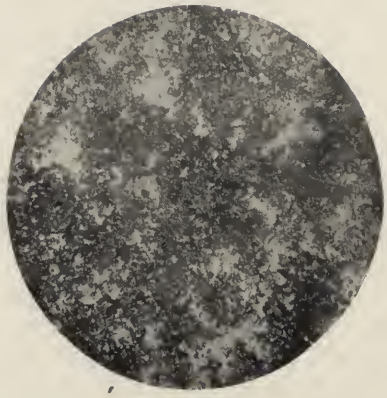
Litharge varies in color from a pale yellow to an orange brown, but the true PbO looks very much like ochre. It is possible that there are other forms of lead oxide with which the paint chemists are at present unacquainted, for it is possible to make a litharge which is relatively bulky and pale yellow. The pigment known as sublimed white lead contains about 20 per cent of oxide of lead, and whether this is a free oxide or an oxysulphate, no one knows at present. Sublimed white lead is pure white, and all investigations tend to show that the 20 per cent lead oxide is a white monoxide. The excellent quality of sublimed white lead as a pigment is partly due to its lead oxide content, and yet the peculiar lead compound which it contains has never been isolated.

Red Lead

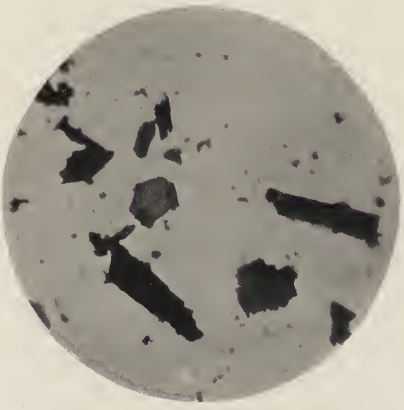
Red lead is a very heavy orange red pigment, more or less crystalline in structure, having a specific gravity of 9.0, and is prepared by heating litharge to a temperature of six to seven hundred degrees Fahrenheit. Owing to the conditions under which it is made, it contains from a trace to an appreciable percentage of litharge PbO, and when used for paint purposes it cannot be said that a small content of litharge does any harm. When prepared in linseed oil it must be freshly used, otherwise it forms a distinct combination with linseed oil and becomes hard and unfit for use. In its physical characteristics it can be compared with plaster of paris. It acts very much like plaster of paris does when mixed with water. Once set it must be reground and



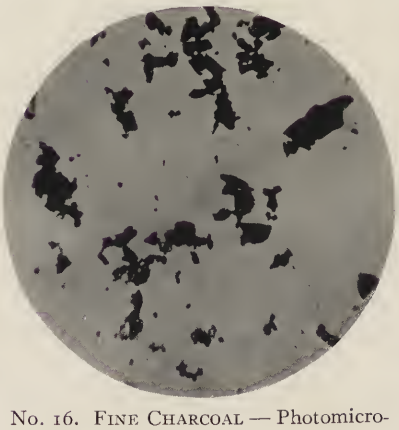
No. 13. Dry Blanc Fixé (Lake Base) — Photomicrograph X300, precipitated from cold neutral solutions; amorphous powder.



No. 14. Silica — Photomicrograph X250, very fine grain; this material has been ground in water.



No. 15. Charcoal Black — Photomicrograph X600, showing hexagonal structure of the wood.



No. 16. Fine Charcoal — Photomicrograph X600.

will never set again. Its use as a priming coat for structural steel has been enormous, but engineers who have studied the subject have come to the conclusion that there are other materials just as good, or better, which are easier to apply and do not possess the characteristic difficulties of application. The author has made many investigations on this subject, and for further detail would refer the reader to "Journal of the Society of Chemical Industry, Vol. XXI, January, 1902," and Vol. XXIV, May, 1905.

Red lead in its pure state is never sold as a mixed paint for the reason just given, although it can be so prepared if the free fatty acids are removed from linseed oil, or if a drying oil other than linseed is specified. There are, however, several good brands of ready-mixed red lead on the market in which the red lead is diluted with silica, clay, and other inert pigments, and from a comparative test it is found that the diluted red leads are every bit as good, and in many instances far superior, to the red lead mixed on the field according to specifications.

The amount of red lead necessary for the production of a proper mixed paint is 33 lbs. dry red lead to one gallon of linseed oil.

As a priming coat it possesses excellent preservative qualities, providing it be properly applied within a reasonable time. If red lead be used in the proportion of 17 lbs. to one gallon of linseed oil it forms a very poor coating on account of the separation of the pigment from the oil, particularly on a vertical surface. In a pamphlet published by a manufacturer a large number of precautions were given to the consumer for the preparation of red lead as a priming coat, the neglect of any one of which might produce failure for the paint. As a prominent engineer remarked, he did not

care to specify a paint in which there were seventeen chances of its failure due to a possible fallibility of human nature. The use of a dry pigment mixed with oil and applied within one hour of its mixture is contrary to the progress of the present day, when paints finely ground by machinery are taking the place of all others. A dry pigment stirred by hand in a pail of oil carries with it a large number of air bubbles which become encysted and carry oxygen and other gases to the surface to be protected. The engineer should, therefore, not specify that a paint should be made entirely of red lead and linseed oil and sent ready for use to the place of application when such specifications cannot be reasonably executed. On the other hand, where red lead is specified the engineer or paint manufacturer who can supply a material containing between 40 and 50 per cent red lead and 50 and 60 per cent inert base is delivering a far better article which can be more easily applied than the undiluted red lead alone.

The author made a large number of experiments on red lead mixed with linseed oil containing a small percentage of drier, applying these mixtures to steel. The mixture was first applied the moment it was thinned, and then at short intervals up to the moment the red lead began to combine with linseed oil so as to make it impossible to handle the brush. The results of the experiment showed that freshly applied red lead was not as good as it was if applied one hour after it was mixed. The paint with which these experiments were made contained 24 lb. red lead to one gallon of paint, which is approximately equal to 33 lb. dry red lead to one gallon of oil. The difficulty in handling paint of this kind is very great, owing to the excessive weight of the paint as carried by the brush. Structural iron painters

all complain that muscular fatigue ensues where undiluted red lead is used, and when the inspector is not watching they will surreptitiously add an excessive quantity of oil, or volatile thinner, in order to lighten their labor, and for this reason red lead has frequently failed, when as a matter of fact it would have proved a perfect success had the original specifications been adhered to. On the other hand, there should be no need of using a protective paint involving such great difficulties when there are dozens of others that are superior, not only from the standpoint of protective influence but also on account of the ease of mechanical application.

It has been mentioned by many writers that one of the serious defects of red lead is the ease with which it is attacked by sulphur gases, but this objection does not hold good where it is properly and quickly coated over with a protective coat of the bituminous class. That red lead in its pure or concentrated state is not as good as a paint containing a solid diluent has been shown time and again where silica, lampblack, graphite, silicate of alumina, and such lighter pigments were mixed with it. Its extraordinarily high specific gravity is very much against its use as a paint, but if a mixture of one pound red lead and one pound graphite is taken, the average specific gravity of the two is equal to that of zinc oxide. Its spreading and lasting power is increased, so that a mixture of this kind is equal to a mixture of any of the good prepared paints for structural steel. Two large exposure tests made by the author in 1899 and examined in 1905 showed that a mixture of 50 per cent red lead and 50 per cent graphite ground fine and mixed in a pure linseed oil containing 5 per cent of lead drier wore almost as well as a mixture of 75 per cent Fe_2O_3, ferric

oxide, 20 per cent silica, and 5 per cent calcium carbonate. The former paint, when the hand was rubbed over it, showed slightly more destruction of the oil, the graphite giving a stove polish effect on the hand. The latter paint also showed a very slight stain on the hand but not quite as marked as the former. The metal underneath both was in a good state of preservation, three coats of paint having been applied. The exposure was on a slanting roof in New York City.

Red lead has had the great advantage of having been the first protective paint ever used, for years no better paint being known. In this respect it is analogous to white lead. Much of the good reputation of white lead is due to the fact that for centuries there was no other white paint, consequently no comparison could be made. It must be borne in mind that all these experimental researches concerning red lead are based on very fine red lead, and no consideration is given to the detrimental reports concerning red lead, due to the fact that it was improperly made and coarse.

A laboratory test of red lead always shows up remarkably well. A steel saucer painted with red lead in the laboratory will demonstrate that this pigment is superior to many others, but a field test of material made according to a laboratory formula and applied on several tons of steel will generally show the opposite, for the obvious reason that in the laboratory a small test is usually carefully applied and little exertion is necessary, either with the mixing of material or for its application. The temperature conditions of the laboratory being normal, the person who mixes the paint usually scrutinizes the result carefully. On the other hand, in the field or at the shop a brush is used, which will do the greatest amount of covering with the least amount of

exertion. The mixture may not be made by the best possible formula, and if it is, more thinning material is generally added until it works freely. The vertical part of the surface will, on account of its position, be more difficult to cover, and the paint will sag or run from it; whereas, the flat plate or saucer-shaped cup used in the laboratory holds the material in place by virtue of its position.

Blue Lead

In the sublimation of Galena a peculiar sulphide of lead is produced, which has been known commercially as blue lead, on account of its blue-gray appearance. This product has been on the market for several years. The contention is that sulphur fumes do not affect it as they affect red lead. As a priming coat it has been well spoken of. Its composition is as follows:

Carbon	2.25	1.73
Lead Sulphate	52.92	49.79
Lead Sulphite	.36	1.44
Lead Sulphide	4.55	4.93
Lead Oxide	37.48	41.34
Zinc Oxide	2.45	1.00
	100.01	100.23

But no correct analyses of this material can be given, owing to the variation in the amount of sulphate, sulphite, and sulphide. The material is not very fine; in fact, it contains an appreciable amount of grit, which, however, is removed in the second grinding.

The pigment is not permanent to light, but in all probability this change in its tone is due to a chemical rather than to a physical decomposition.

CHAPTER IV

The Red Pigments

The red pigments used in the manufacture of mixed paints are principally the oxides of iron, the red oxides of lead, and the permanent vermilions. No space will be devoted to the sulphide of mercury (quicksilver vermilions), as the use of these materials has been superseded entirely by aniline or para-nitranaline vermilion. Likewise no attention will be paid to the sulphide of antimony reds, as they are obsolete in paint manufacturing.

Among all the red pigments in the paint industry, the oxides of iron take the lead as by far the most useful. Several years ago the author called attention to the fact that various forms of ferric oxide having the formula Fe_2O_3 could be used as rubber pigments. The sulphur used in the vulcanizing of rubber had no effect on the ferric oxide, no sulphide of iron being formed in the combination. On investigation it was found that some forms of ferric oxide are remarkably stable in composition, acting in many regards like a spinel. Exhaustive tests made with some of the ferric oxides used as paints for the protection of steel and iron show that they are far superior to red lead and to graphite as paint protectors, being midway between the two in specific gravity. A mixture of graphite and ferric oxide

containing 75 per cent Fe_2O_3 and 25 per cent silica outlasted graphite by two years and red lead by three years. These tests were made on horizontal roofs, and eliminating the question of the cost of the paints, the ferric oxide stood the test and was the cheapest in the end. No argument can be adduced that ferric oxide is a carrier of oxgyen, for it is a complete chemical compound, is not readily acted upon by dilute acids, not affected by alkalis nor by sulphur gases, and as a paint the author has not been able to demonstrate that it reacts on linseed oil.

All of these arguments refer, of course, to a ferric oxide of known purity and definite composition either as pure Fe_2O_3 or as Fe_2O_3 containing 25 per cent silica. In the course of its manufacture from the waste products or wire mills, for instance, or direct from ferrous sulphate, the processes being analogous, there is a likelihood that a small percentage of free sulphuric acid may cling mechanically to the substance. A good sample boiled with water and tested with methyl orange will demonstrate this defect. It is wise, therefore, under all circumstances to add up to 5 per cent calcium carbonate in any or all of these ferric oxide paints. There is, however, another ferric oxide made from Persian ore. Over one hundred analyses of this ore in the laboratory of the author has shown that its composition will not vary more than 2 per cent either way, it being 75 per cent Fe_2O_3 and 25 per cent SiO_2.

Venetian Reds

Venetian reds have sometimes been described as burnt ochres, but this definition of the Venetian reds is incorrect. The generally accepted composition of the Venetian red is

a combination of ferric oxide and calcium sulphate, in which the ferric oxide will run from 20 to 40 per cent, and the calcium sulphate from 60 to 80 per cent. When ferrous sulphate is heated with lime an interchange or reaction takes place, the sulphuric acid of the copperas going to the lime while an oxidation of the iron takes place. Another method known as the wet method is the direct reaction between ferrous sulphate and wet slacked lime.

Venetian red has been known as a paint pigment for upwards of a century, and while theory would indicate that it is by no means as desirable a pigment to use as other mixtures of ferric oxide, it must be apparent that in view of the fact that it has given general satisfaction it is by no means as undesirable a pigment as chemists indicate. The tendency, however, at the present time is for manufacturers to buy strong pure oxides and reduce them with other inert fillers, for the principal reason that a Venetian red carrying a high percentage of calcium sulphate and an unknown quantity of water or moisture tends to become hard in the package, whereas the mixtures of known composition remain soft for many years. Venetian reds are all of the familiar brick color shade, the color of bricks being caused by the same pigment as the one that gives the color to Venetian red.

Indian Red

This is supposed to have been named by Benjamin West, a celebrated American artist who lived more than a century ago, and who as a boy used a few primary earth colors as pigments for paint. One of these was a natural hematite, and he observed that the Indians used this for painting their

faces. The name is also supposed to have had its origin in the fact that "Persian Gulf Ore," which was found in the Orient, was exported to England under the name of "East Indian Red." This Persian Gulf Ore is likewise a hematite, and later on a similar ore was found in parts of England which, when mined, looked very much like coal, but when crushed and ground in water turned a deep blood red. The old name for this mineral is still "blood-stone," and some very fine specimens of this mineral are still mined in England in conjunction with beautiful quartz crystals, so that we find in England a careful selection.

The native Indian red will run 90 per cent Fe_2O_3, the American 88 per cent, and the Persian 75 per cent, the balance in every case being silica. The Indian red of commerce, however, is an artificial product made like the base of the Venetian red by calcining copperas and selecting the product as to shade. There is no pigment, with possibly the exception of lithopone and artificial barium sulphate, which will approach Indian red in fineness of grain. The prices which a fine, pure Indian red or ferric oxide of any shade will command is most remarkable, many tons being sold every year in large quantities at as high a price as fifty cents per pound, and used entirely for polishing gold, silver, and other metals. The well-known "watch-case rouge" is nothing but pure Indian red which has been ground, washed, and treated mechanically with so much care that three quarters of its selling price is represented in the labor of manipulation. If it is therefore accepted that a fine ferric oxide be mixed with linseed oil it can be easily seen from the nature of the physical characteristics of the pigment that a remarkably good result is obtained.

Permanent Vermilion

It may be of interest to the chemist unacquainted with the manufacture of dry colors to know that English vermilion (sulphide of mercury), of which the prototypes are Chinese vermilion, American quicksilver vermilion, etc., was formerly used wherever a permanent red was desired, and particularly for railroad work was this vermilion the only red that could be used, for it did not fade. It, however, has the disadvantage of darkening in the light and eventually turning brown. The real sulphide of mercury is black and the red sulphide of mercury is a forced compound. The mineral cinnabar, which has the composition just described, is also red, but not very bright, and that found and made in Austria, known as Trieste vermilion, has always been regarded as the most permanent of these sulphide of mercury reds. Mixed paint manufacturers do not use it, and in fact paint manufacturers generally have discarded it, for the reason that the so-called para-nitranaline reds are better, cheaper, and more permanent.

In order that the chemist may understand the composition of the para-vermilions, a complete formula is given for its manufacture.

Para-Nitranaline Lake

Naphthol Solution

15 grams Beta Naphthol or Beta Naphthol R.; 30 grams Caustic Soda Lye 22° Be.; 10–20 grams Para-Soap P.N.
(In sufficient boiling water to dissolve thoroughly).

Diazo Solution

14 grams Para-Nitranaline dissolved in boiling water; 25 grams Hydrochloric acid 20° Be.; 200 grams Ice.
When the solution is cooled to 32° to 35° F., add very slowly, while

stirring constantly, 34 grams nitrite of soda solution (29 gms. nitrite in 100 gms. cold water).

Allow to stand 15 to 20 minutes. Then add slowly 35 grams acetate of soda previously dissolved in cold water.

To the naphthol solution add the base you intend to use. 250 grams of Blanc Fixe' give good results. For bluer shades use Beta Naphthol R. For yellower shades use Beta Naphthol.

When these colors have been precipitated on an orange mineral base they have been known to catch fire spontaneously in the drying-room, and therefore great care should be exercised in their manipulation with lead bases.

There appears to be a difference of opinion among consumers as to whether these reds are really permanent or not, and careful investigation reveals the following: the para-vermilions are soluble in linseed oil, and therefore even when a pigment contains only 5 per cent tinctorial matter it is useful and effective as a red paint. White lead in any form mixed with a para-red destroys its color and turns it brown. A few years ago when this color first appeared on the market it frequently happened that it turned perfectly white when exposed to the air, but when it was rubbed with raw linseed oil it turned a brilliant red again, and a microscopic examination showed that the film had been entirely encrusted with very fine crystals of sodium nitrite and other salts that had not been completely washed out of the lake pigment, and so para-red obtained a bad reputation, not due to the color, but due to the ignorance of the manufacturer.

Para-red has penetrative powers in both directions; when painted, for instance, on a sheet of cloth for sign work, it will penetrate through and stain the under side yellow. If white lead paint be lettered over it, it acts the same and turns white lead yellow, or a yellowish brown.

Enormous quantities of this vermilion are made every year, and so strong is this color that average analyses of the paint used for agricultural implement purposes will show the pigment to be composed of 90 per cent barytes, 5 per cent para-red, 5 per cent zinc oxide or zinc sulphide. Its presence in mixed paints is very easily detected by boiling with varnish solvents and noting the peculiar orange color of the filtrate.

CHAPTER V

YELLOW AND BLUE PIGMENTS

Burnt Ochre — American Sienna

This is a reddish yellow pigment containing approximately 60 per cent ferric oxide and 40 per cent silicate of alumina or clay. It is not very largely used as a paint pigment, as its color is muddy when compared with Venetian reds. Burnt sienna is similar in composition to burnt ochre except that the percentage of ferric oxide is slightly higher, it often ranging as high as 70 per cent. It is, however, much more transparent or translucent than ferric oxide, its shade being a characteristic mahogany. Its chemical composition is described under the head of raw sienna, the earth from which it is made. In America a grade of sienna known as American sienna is found, which, when burnt, is largely used for the making of structural iron paints of the brownish red shade. These paints while rather difficult to grind give excellent results. No standard of composition can be given, as most of them vary in the percentage of iron they contain.

Chrome Yellow

Chrome yellow is a lead chromate of medium shade, as precipitated from a solution of nitrate of lead and potassium bichromate. The lemon or lighter shades are made from solutions acidified with organic or inorganic acids. An

organic acid such as citric acid, which forms a lead citrate, changes the shade, producing a greenish lemon, which may vary from a greenish lemon to a brilliant canary, particularly if sulphuric be added. If an alkaline solution of potassium bichromate be used an orange precipitate is produced, so that a great variety of shades of this pigment can be obtained.

All of the chrome yellows are perfectly permanent, provided they are thoroughly washed to free them from residual salts. Manufacturers are now abandoning the old mechanical method of stirring chrome yellow after it is precipitated, and are substituting air stirring which avoids any possible tendency to produce lead sulphide, the air converting the sulphide into sulphite and sulphate. Chrome yellows when thoroughly washed are permanent to light, but they cannot be recommended where sulphur vapor is generated, owing to the formation of lead sulphide, traces of which detract from the brilliancy of the color of the pigment.

The composition of chrome yellow is as follows:

LIGHT CHROME YELLOW

$$PbSO_4 + PbCrO_4$$

or,

$$2PbCO_3\ Pb(OH)_2 + PbCrO_4$$

or,

$$PbCrO_4 + \left.\begin{matrix}\text{Citriate}\\ \text{Tartarate}\\ \text{or Sulphate}\end{matrix}\right\}\text{of Lead}$$

MEDIUM CHROME YELLOW

$$PbCrO_4$$

ORANGE CHROME YELLOW

$$PbO\ PbCrO_4 = Pb_2CrO_5$$

Ultramarine Blue — Cobalt Blue

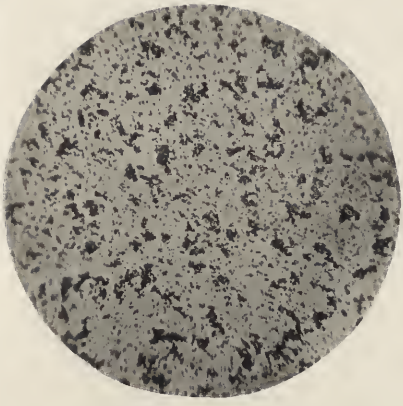
Ultramarine blue is one of the most wonderful pigments made. It is perhaps the first synthetic color ever manufactured. The natural ultramarine blue is a mineral (lapis lazuli) which is found in Siberia, Persia, and China, and is used for decorative purposes only. It was formerly used for painting, and is a perfect pigment although it has very little body. In 1828 both Grunnet and Gmelin of France succeeded in making an artificial ultramarine blue which equaled lapis lazuli in composition. It is a very strange fact that the substances from which ultramarine blue is manufactured possess none of the characteristics of the finished material. Briefly stated, when a mixture of china clay (aluminum silicate), sodium carbonate, sodium sulphate, sulphur, and charcoal is heated a brilliant blue is produced which is largely used as a wash blue in making blue paper, printing inks, and as a permanent pigment for house painting. It cannot, however, be used in conjunction with white lead, because the sulphur it contains is likely to blacken the lead. It is a non-poisonous color, and is also used for whitening refined sugar. Ultramarine blue and Prussian blue work well with zinc.

Artificial Cobalt Blue

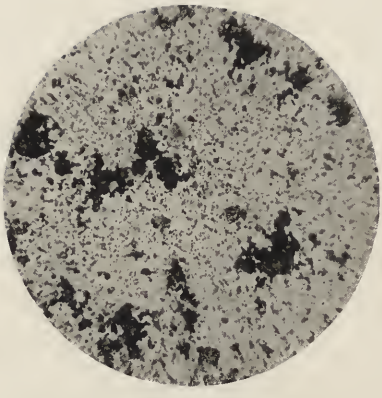
The cobalt blue of commerce is the same as ultramarine blue, the difference being in the shade. Ultramarine when mixed with thirty parts of a white pigment, such as zinc oxide, produces a violet shade, whereas the cobalt blues when mixed in the same proportion produce a turquoise or sky-blue shade. Chemically the composition of these ultramarines and cobalts will average about 50 per cent silica,

25 per cent alumina, 15 per cent sodium sulphide, in combination with 3 per cent water and 10 per cent sulphur. The addition of the slightest trace of acid to a paint containing ultramarine blue liberates H_2S, which always indicates the presence of ultramarine in the blue, or bluish pigment. Under the microscope ultramarine blue has a distinct crystalline appearance. When these crystals are badly destroyed by fine grinding the color suffers very much, the characteristic brilliant blue of ultramarine becoming an exceedingly muddy shade. Its tinctorial power is very weak, but it is exceptionally permanent to the light. In blue shades of mixed paints the percentage of ultramarine blue can be determined either by difference or by the percentage of sulphur present. If 10 per cent is accepted as the amount of sulphur in ultramarine blue a fairly accurate quantitative determination can be arrived at. Where ultramarine blue is mixed with lithopone the zinc sulphide of the lithopone as well as the ultramarine evolve H_2S. When determining the ultramarine, the total H_2S evolved must be calculated as sulphur. The zinc must be precipitated as carbonate and weighed as oxide and calculated to sulphide. The sulphur in the ZnS must then be deducted from the total sulphur. From the difference the percentage of ultramarine blue in the original pigment may be calculated. As acetic acid liberates the H_2S from the ultramarine but does not attack the S in lithopone, this acid may be used and the percentage of sulphur in the ultramarine determined directly.

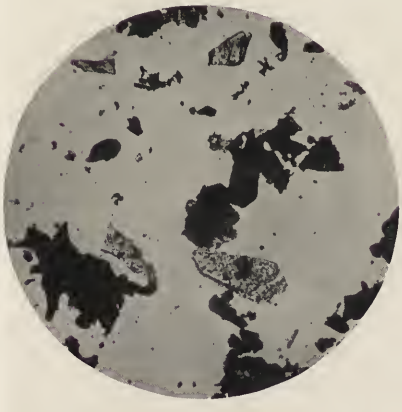
Ultramarine blue reacts with corroded white lead but not with zinc oxide. It does not react very quickly with sublimed lead or zinc lead, but for the making of pale blue shades, which should remain permanent in the package, zinc oxide is to be recommended in preference to any other



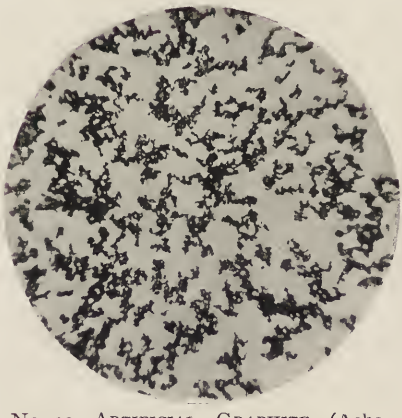
No. 17. Wood Pulp Black — Photomicrograph X500, very fine uniform grain.



No. 18. Vine Black (German make) — Photomicrograph X250, two sizes of grain.



No. 19. Natural Graphite — Photomicrograph X250, containing about 40 per cent of Silica, showing crystals of Silica and Graphite.



No. 20. Artificial Graphite (Acheson) — Photomicrograph X250, uniform in grain.

white pigment. Ultramarine blue should not be mixed with any of the chrome yellows or chrome greens, because a darkening effect is sure to take place. Ultramarine blue behaves very badly with linseed oil containing an excessive amount of lead drier. For mixed paints of pale tints, a resinate of manganese or oleate of manganese drier is to be recommended. Most of the Japan driers contain large quantities of lead, and a white Japan composed of rosin, manganese, and linseed oil will make the most permanent mixture.

Prussian Blue

(Synonym: Milori Blue, Bronze Blue, Antwerp Blue, Chinese Blue, etc.)

Almost every text-book on elementary chemistry gives a description of Prussian blue which is a ferro-ferri cyanide of iron, and in a general way it can be produced for laboratory purposes by the simple mixture of ferro cyanide of potassium and a ferric salt of iron. Commercially the well-known ferric iron reaction of analytical chemistry is reproduced on a large scale. Prussian blue, however, is made from a ferrous salt and is obtained by the mixture of ferrous sulphate (copperas) and ferrocyanide of soda (yellow prussiate). This mixture produces a pale bluish white flocculent precipitate, and the chemist will easily understand how, with the addition of any oxidizing agent, such as bleaching powder, potassium chlorate, etc., the precipitate is converted from a bluish white into a dark blue pigment. There are a number of varieties of Prussian blue, all approximating this composition but made differently, being sold under the names of Steel blue, Milori blue, Bronze blue, Antwerp blue, and Chinese blue. Although each of these blues is chemi-

cally the same as Prussian blue they have different physical characteristics. Prussian blue, for instance, is like a mixture of indigo and black in its dry state, and when tinted with one hundred times its own weight of zinc oxide the shade produced is a muddy violet. Chinese blue when treated in the same manner gives a purer blue which has no trace of violet in the shade. The steel blue when diluted one hundred times gives a turquoise shade. And so for the manufacturer of pale blue shades the tones of these blues must be taken into consideration.

There is much discussion among paint manufacturers as to whether Prussian blue is a permanent pigment or not, and the author is frank to say that this matter can be decided as follows: Prussian blue, or any of its allies, may be considered permanent or fugitive, according to the manner in which it is made and according to the base with which it is mixed. If Prussian blue contains more than a trace of soluble salt (sodium sulphate) it has a decidedly yellowing action on the oil, and a light blue or light green made of such Prussian blue is supposed to be fugitive. On the other hand, a number of experiments made with thoroughly washed Prussian blue have demonstrated that it is a perfectly stable color and does not change its shade. As a tinting color for making pale blues in mixed paints, Prussian blue has caused an enormous amount of trouble. A pale blue mixed paint that is composed of white lead in any proportion changes color in the package, a reduction process taking place which converts it from a ferric into a ferrous state, so that when a can of light blue mixed paint made with Prussian blue and white lead is opened it is a sickly green instead of a blue. If such a paint be applied to an exterior surface, it is completely converted into its

original blue shade as soon as it is dry. The zinc oxide paints have the same action but to a very much smaller degree, and a paint manufacturer who desires to make a pale blue by the use of Prussian or Chinese blue must avoid the use of white lead in his paint. The artificial cobalt blue mixed with zinc oxide is, however, more desirable.

Prussian blue is also used in small quantities for mixing with bone black to produce intensely black shades.

It is a simple matter to determine the presence of prussian blue in any pigment by the addition of caustic soda to the dry extracted pigment, warming, filtering, and testing the filtrate with a drop of ferric chloride after acidifying. The Prussian blue made in laboratories will contain approximately 30 per cent of iron, so that if an analysis is made of a mixed paint tinted with Prussian blue and the percentage of iron is multiplied by three, a fairly correct estimate of the percentage of Prussian blue is obtained; and while the factor given cannot be absolutely correct, owing to the difference in the various blues made, it is so nearly correct that a synthesis made from such an analysis has invariably given the same shade.

Chrome Green

Chrome green is sold under various proprietary names, and must not be confounded with the oxide of chromium. Chrome green is essentially a mixture of Prussian blue with chrome yellow, but the chrome greens, unless chemically pure, are always mixtures of blue and yellow on a barytes base. A green paint made entirely of Prussian blue, chrome yellow, and an inert base such as silica or barytes, is very easily analyzed by ignoring the pigment and weighing the base, calculating the pigment by difference. This is, how-

ever, not a desirable method to recommend except in the hands of an expert who knows that the pigment or paint is made on an inert base. Inasmuch as there is a great variety of shades of chrome green, ranging from a yellowish green to a very dark olive, and as the dark shades may be composed of either a mixture of orange chrome yellow, and Prussian blue, or a light chrome yellow and Prussian blue and black, it is not safe to multiply the percentage of iron by a factor to obtain the percentage of Prussian blue, because many shades of green are produced with the use of ochre. The iron factor would, therefore, be misleading. The lead chromate can be washed out with hot hydrochloric acid and will precipitate on cooling. The Prussian blue may be washed out with a caustic alkali solution, the iron being left behind, but it can be reprecipitated as Prussian blue with a ferric salt, the necessary amount of chrome yellow and Prussian blue originally used being thus recovered. This method is uncertain only when an olive yellow is being analyzed.

Chrome green should never be mixed with white lead for the pale shades, as it changes color in the can in ratio to its content of Prussian blue. Zinc lead, zinc oxide, sublimed lead, or lithopone should therefore be used. If chrome green is not well washed the soluble salts are likely to affect the linseed oil. At the seashore the salt atmosphere invariably attacks chrome green and bleaches it, and where an absolutely permanent green is required, chromium oxide should be used.

Chromium Oxide

Chemical Formula, Cr_2O_3.

This green is one of the most permanent greens used, but it is not extensively used in the manufacture of mixed paints excepting where absolute permanence is necessary. It is met with occasionally in railway paints for switch target signals, and as a mixed paint to be used on vessels for repainting the receptacle in which the port light rests. It is not a brilliant green and cannot be compared with the chrome greens, which are mixtures of chrome yellow and Prussian blue. It is more of an olive shade.

CHAPTER VI

The Black Pigments

The principal dry pigments used in making black paint are bone black, and its varieties, lampblack, carbon black (or gas black), graphite, mineral black, charcoal, and powdered coal.

There are quite a large variety of bone blacks beginning with ivory black and going down to the by-product of the sugar mills known as "Sugar House black." In composition all of the animal blacks are alike, in so far as they always contain carbon and calcium phosphate. The carbon varies between 15 and 23 per cent, the difference being phosphate of lime and moisture. Some of the best blacks used for mixed paints are made from the shin-bone and skull of the sheep, it having been found that these blacks are of the most intense color. Occasionally variable amounts of calcium carbonate are found in these blacks, depending largely upon the length of time the bone was burned. For making a very intense and good quality black which will not settle when mixed with varnish, carefully selected bones are taken, or burnt ivory chips, and digested in hydrochloric acid which removes all the lime salts and leaves the carbon as a flocculent residue. This carbon is probably the highest priced and most intense black used by paint makers and is frequently sold under the name of black toner, because it sometimes is used for giving an intense tone to an other-

wise pure black. In the article known as "Black color in varnish," it is found that black toner serves its purpose best, and a black paint which is composed of black toner ground in linseed oil and reduced with a very high grade of coach varnish is worth from $4 to $6 per gallon.

Lampblack

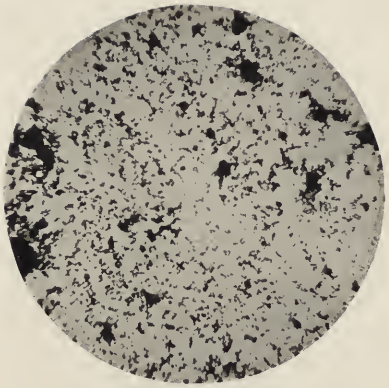
Lampblack is the condensed smoke of dead oil, and while it may be made from a variety of raw materials it is made principally from the petroleum oils for which very little other use has been found. It has been observed among chemists that lampblack can be made of varying specific gravity, while its composition is very uniform and averages 98 per cent carbon. As a paint pigment it has remarkable qualities, and among the practical painters it is regarded as the most permanent, due to its exceptionally fine state of subdivision. In America it has been very largely used as a sign painter's black, and wherever it is painted over another paint in the form of letters directly on the wood or metal the surrounding paint disappears gradually, until after a lapse of years nothing is left but the lampblack paint, which remains behind sometimes in bold relief. In color it is a distinct gray, and while it may sound ridiculous, it is true that a sign can be composed entirely of lampblack, the background being painted with ivory black and the lettering made with lampblack will show up clearly and distinctly; so by way of comparison it may be said that lampblack will make a light mark on ivory black. The practical paint man will always recognize lampblack on account of this peculiar gray tint. The one serious objection to the use of lampblack in a paint is the fact that owing to the peculiar

process of its manufacture it is very likely to carry over some condensed hydrocarbon oil. As small a fraction as less than 1 per cent of this unburnt or condensed oil will retard the drying of lampblack to such an extent as to make it at times unfit for use. The author carefully worked out both the cause and remedy of the non-drying qualities of lampblack, and inasmuch as such large quantities of blacks similar to lampblack, which dry very poorly, are being used, the following treatment of lamp black must be considered.

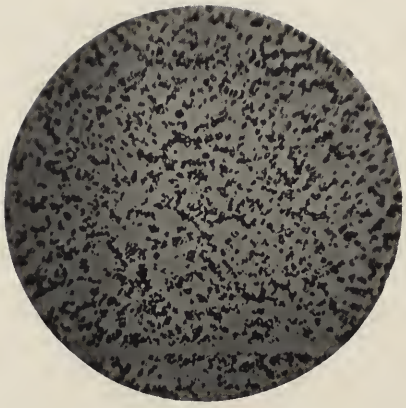
In the laboratory the method of determining the amount of oil in lampblack usually consists in taking a weighed amount of lampblack, placing it in a filter and washing it two or three times with 62° naphtha. The black is then dried in an air bath and weighed. The amount of loss is calculated as grease, care, of course, being taken to extract the moisture before treating it for these oils. On experimenting with these extracted samples, it was found that when mixed with a drying oil and placed in the sunlight, lampblack would dry free to the touch within twelve hours. The removal of the unburnt or condensed oil is therefore essential to making a quick-drying black. A very simple apparatus can be made in which ten or fifteen barrels of lampblack can be washed per day, and the benzine used for this purpose is just as good for making the low-priced asphaltum varnishes as benzine would be that did not contain any impurity.

Carbon Black

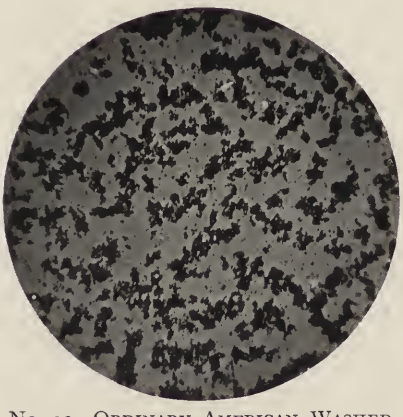
Carbon black is in all respects similar to lampblack, except that it is intensely black in color, and while it shows no crystalline structure under the microscope it condenses itself so hard on the places from which it is scraped that it



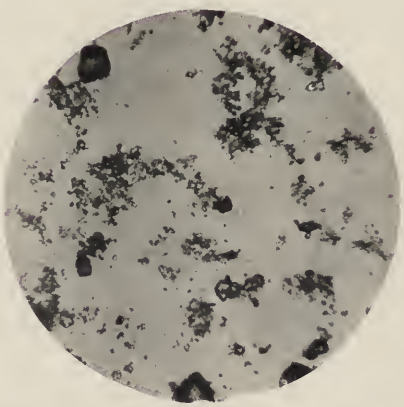
No. 21. Artificial Graphite (Acheson) — Photomicrograph X250, containing 90 per cent of carbon.



No. 22. American Washed Ochre — Photomicrograph X250, of the same composition as French Ochre.



No. 23. Ordinary American Washed Ochre — Photomicrograph X250, powdered and bolted; lower in iron than the French, but of uniform grain.



No. 24. J. F. L. S. Ochre — Photomicrograph X250, showing crystalline structure.

is largely interspersed with flakes of black which to all appearance are crystalline and are very refractory in the mill. Its tinctorial power is very great, one pound being sufficient to tint one hundred pounds of white lead to a dark gray. Paint manufacturers have, however, abandoned its use as a tinctorial material for several reasons, the principal ones being that it is likely to produce a streaky color when used as a tint, owing to the presence of very small nodules that do not show up until it is applied as a paint, and these streaks cannot be brushed out, and that in the second place it shows a peculiar tendency to attach itself to minute air bubbles, so that when made into a mixed paint of a lighter tint which has been standing in the package for a considerable time, fairly large amounts of black rise to the top of the liquid, which can only with difficulty be made of a uniform tint.

There are a variety of other carbon blacks made by the burning of acetylene, benzol, crude tar liquor, paraffin oil, etc., but these are analogous to carbon black.

Graphite

Synonym: Black Lead, Stove Polish. Specific Gravity, 1.19 to 2.5, depending upon the impurities contained in it.

Graphite is found as a mineral almost all over the world. It is very largely used as a paint pigment, and it is remarkable that in its natural state it has all the defects of bulkiness which red lead has for weight. The purer a paint pigment is as to its contents of carbon the poorer is the paint produced. If graphite be taken with a content of 80 or 90 per cent carbon and mixed with linseed oil, it forms a porous, fluffy film, and the particles of graphite coagulate in the linseed oil and

produce a very unsatisfactory covering. If graphite be diluted with a heavier base, its weakness then becomes its strength and a very good paint is formed. Many of the characteristic chemical and physical defects of red lead are largely reduced and frequently eliminated when it is mixed in proper proportion with graphite, a high grade of graphite when finely ground with linseed oil acting as a lubricant and sliding under the brush.

Pure graphite, as is well known, will cover from 1000 to 1600 sq. ft. to the gallon. Such a paint film is so exceedingly thin that, while it looks good to the eye, in a short period decomposition more easily takes place beneath it than beneath many poorer paints. It is, therefore, essential to reduce graphite with a heavier base, and to this end it has been found that a mixture of silica and graphite produces very good results; but even this paint has the objection of having too much spreading power.

Misnomers have crept into the paint trade in regard to graphite paints, such names as green graphite, red graphite, brown graphite, etc., being in use; when in reality such graphites do not exist, excepting as far as graphite has been mixed with pigments of these colors. A six-year test of a linseed oil paint made with a neutral ferric oxide, containing in its composition 75 per cent ferric oxide and 20 per cent silica mixed with graphite containing 85 per cent graphitic carbon, has proved itself to be as good a paint as can be desired for ordinary purposes. The pigment in a paint of this kind will withstand the chemical action of gases and fumes, but the oil as a vehicle is its weakest part.

Since the electro-chemical industry has been developed at Niagara Falls graphite has been made artificially and is sold under the name of "Acheson Graphite." This graphite

is to be commended as a paint material on account of its uniformity and fineness of grain, but it should not be used entirely alone as a pigment, for as such it possesses the physical defects of lightness just described. A graphite paint containing more than 60 per cent graphite does not serve its purpose very well unless the 40 per cent of heavy pigment added to it be a lead or a zinc compound. A rather unfortunate defect in the graphite paints containing large amount of graphite is the smooth and satin-like condition of the paint film, which is poorly adapted for repainting. It has often been noted that a good slow-drying linseed oil paint will curl up when applied over certain graphite paints, because it does not adhere to the graphite film. On the other hand, if particular forms of calcium carbonate, silica, or ferric oxide are added to graphite a surface is presented which has a "tooth" to which succeeding films adhere very well.

The question of coefficiency of expansion in paints has not been thoroughly considered, and many a good paint will fail because it is too elastic. Engineers sometimes prefer a paint which when scraped with a knife blade will curl up like ribbon. Priming coats suffer very much when they are as elastic as this, but the paint chemist can overcome these defects by the proper admixture of inert fillers and hard drying oils.

Graphite is known as a very slow drier, but this is true only when too much graphite is used in the paint. There is no reason why a graphite paint should not be made to dry sufficiently hard for repainting within twenty-four hours.

Charcoal

It is not generally known that charcoal from the willow, maple, and bass trees is largely used as a pigment for black paints. There are a number of black paints on the market which are composed of charcoal, lampblack, litharge, and linseed oil in varying proportions, and in the early history of these paints it was difficult to make them so thin they would not turn semi-solid in the package. It was found that as a preservative coating on steel they did remarkably well. Investigations by the author have shown that this preservative action is accidental and is due entirely to the alkali contained in the charcoal. Some of the charcoal used is a by-product from paper mills and contains as high as 2 per cent potassium carbonate. In fact, the carbonate is produced by the burning or calcining of wood, most charcoal being more or less alkaline. In the examination of paints of this character it was noticed that the spectroscope showed the potash lines, and thus it became a very simple matter to determine by means of the spectroscope whether a paint was a charcoal paint or not. The author has demonstrated on previous occasions that the oxidation of metal cannot take place in the presence of certain alkalis, and therefore these charcoal paints when freshly made are excellent preservatives for the metal. But, inasmuch as moisture is always present in these paints, having been added in the form of water or contained in the raw materials, saponification takes place more or less rapidly, so that the paints are sometimes unfit for use two months after they are made.

Coal

Powdered anthracite and bituminous coal are likewise used in black paints, but the origin of their use is due to some extent to poorly written paint specifications. An engineer will at times prescribe a paint containing a certain percentage of ash, and in order to meet this requirement a paint manufacturer will have to add coal in order to conform with the requirements; as sulphur compounds such as So_2 and So_3 always exist in coal, a paint is produced which is exceedingly harmful to metal.

Mineral Black

Mineral black is usually composed of heavy black slate, more or less finely ground, and as a paint pigment is inert. It is often toned with lighter carbons and lampblacks and is not largely used on account of its destructive action on paint mills. Where iron paint mills are used these mineral blacks are found to be very expensive, because they will dull the sharpest mill in a few hours' run. As they possess very little tinctorial power, it is more advantageous to use a 200-mesh silica.

Vine Black

In all essentials this pigment is the same as the powdered charcoals for paint purposes, excepting that the grain is smaller and the black denser. It is made by charring the grapevine in Germany. If overcharred it is likely to become alkaline. The same tests may be applied to this black which were used for all the charcoal and wood pulp blacks, the simplest and most effective test being to boil the black in water, filter, and add a few drops of phenolphthalein.

The Inert Fillers and Extenders

Very few mixed paints are made of a concentrated pigment, for it has been found in practice that a concentrated pigment is frequently too heavy to be used alone, as in the case of white lead, or it is sometimes too bulky and too light, as in the case of graphite or lampblack.

Then again, the wearing quality of the pigment alone is very seldom equal to that of the diluted pigment, and an erroneous term has crept into the paint trade with reference to the concentrated pigment, so that these pigments are frequently called pure pigments. But many of the more progressive manufacturers and consumers are realizing that purity with regard to a color is a term which is very strictly applied to its tone rather than to its chemical composition. As an evidence of this, a pure ochre, as it is known in the paint trade, contains naturally 80 per cent of inert filler; a pure and expensive coach black often contains as much as 85 per cent of inert extender, and conversely a chemically pure barium sulphate (which would contain 100 per cent barium sulphate) is unfit for any paint purpose when used in its so-called state of purity. These examples can be carried out to a great length, but they all serve to show the same tendency. This question has been definitely settled by the consumer and the manufacturer. In the early stages of the paint industry the tendency was towards using concentrated colors, but practical experiments showed that when these pigments were diluted or extended with inert materials they not only made better paint from a practical standpoint, but the paint was very much more durable and frequently presented physical characteristics which demonstrated the value of such a mixture.

There are a large number of these extenders, and no single one of them is applicable to all paints, and there are times when one is superior to another, and yet for commercial reasons the manufacturer of barytes will always contend that barytes is superior to silica; and the manufacturer of silica will always contend that his material is superior to calcium carbonate, and so on until the point of beginning is reached. The fact, nevertheless, remains that for wooden structures one filler has an advantage over another; for steel structures a number of fillers are equally as good, and for the painting of masonry, a pigment which contains natural fillers is desirable.

The principal fillers used which will be thoroughly explained in the following chapters are as follows:

1. Barytes.
2. Barium sulphate.
3. Barium carbonate.
4. Silica and its various forms, infusorial earth, etc.
5. Calcium carbonate.
6. Whiting.
7. White mineral primer.
8. Clays, silicate of alumina.
9. Kaolin.
10. Asbestine.
11. Calcium sulphate.
12. Gypsum.
13. Charcoal.

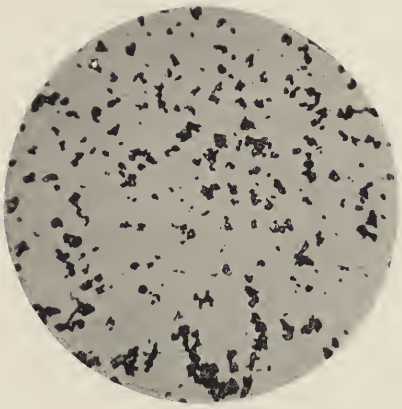
CHAPTER VII

Silica and Clay

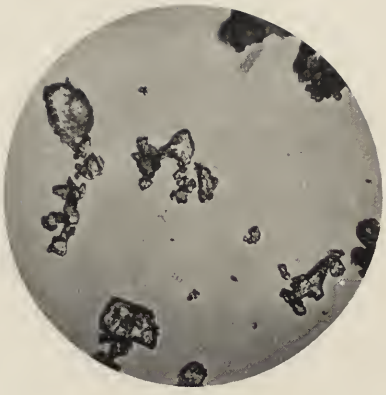
Silica = SiO_2; Synonym = Silex; Infusorial Earth.

The introduction of silex in paint is due to the researches and investigations made by David E. Breninig, M.D., who in the early fifties had noted that when white lead was mixed with barytes it stood exposure better than pure white lead. Late in the fifties he came across some rock crystal quartz and, on grinding and mixing it with white lead, found that it improved the paint. The preparation of silica, especially for the paint trade, became an established industry between 1865 and 1870.

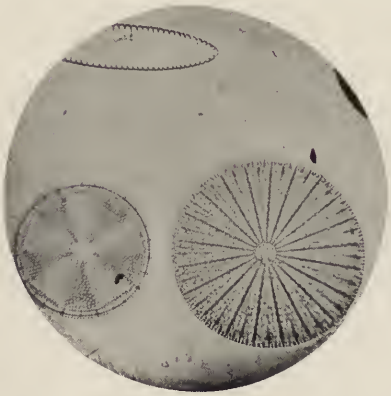
The earlier process for powdering quartz was the simple and economical method of dry grinding by the tumbling process. The quartz was simply crushed to a granulated state and then put in a tumbling barrel with pebbles which was revolved until the silica was reduced to a comparatively impalpable powder. It was, however, found that this method was not satisfactory because it did not produce uniform results, and the Silex Lead Company, which had been formed for the manufacture of silica or silex for the paint trade prior to 1870, adopted the process of heating the quartz to a visible red heat, plunging it into water and crushing it after the sudden change of temperature had split the silica into a finer state of division. The silica was ground in tubs under water with stone bottoms and drag stones, and after it had been thoroughly comminuted it was



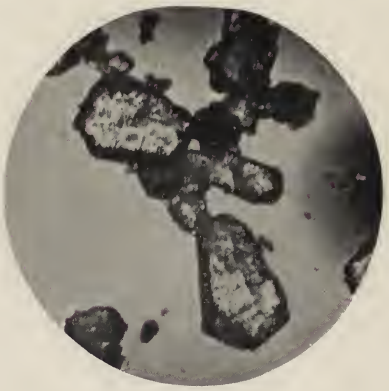
No. 25. American Burnt Sienna — Photomicrograph X250, excellent quality, uniform grain.



No. 26. Calcium Sulphate (Gypsum) — Photomicrograph X250 (American).



No. 27. Diatoms — Photomicrograph X600, frequently found in Whiting.



No. 28. Terra Alba (French Gypsum) — Photomicrograph X600, showing crystalline structure of Calcium Sulphate.

washed, floated, dried, and then bolted to a given degree of fineness. There can be no question that the preparation of silica in this manner produced a material of great uniformity, the value of which in paint is unquestioned. In the early part of the seventies the first practical tests were made on the coast of Maine. It was found that pure white lead would not stand the exposure of the seashore more than a year. At the end of this time it resembled whitewash and presented a poor surface for repainting. A mixture was made at the same time of one third silica prepared by heating and washing, one third zinc oxide and one third white lead. These materials were ground together in pure linseed oil and sufficient drier added. At the end of seven years this paint was still in good condition and presented an excellent surface for repainting.

Silica like many of the inert materials has the added physical advantage of presenting what is known as a "tooth," which fits it exceedingly well for repainting. Silica is inert as an extender or filler in paint, and does not combine with any other pigment or vehicle. The detection of silica in mixed paints is very easily accomplished by means of the microscope and Nicoll Prism, as the metallic pigments do not polarize. In chemical analysis we often find 1 per cent of silica in an otherwise pure paint. This 1 per cent of silica would generally show up in large arrow-head crystals entirely scattered throughout the field of the microscopic vision, and are due to very small particles of silica which have been worn off from the grinding stones of the mill. The amount of silica which may be safely added to a mixed paint without detracting from its covering property, and which will increase its wearing quality, is one third of the total pigments used.

The composition of the various silicas on the market is quite uniform, and those that are made from clear colorless quartz, or faintly colored quartz, are practically free from iron. Silica made from rock quartz will assay 99.7 SiO_2.

Infusorial earth is almost pure silica and is largely composed of the skeletons of diatoms. It is exceedingly bulky and is used by some paint manufacturers to prevent the settling or hardening of paint in cans, and owing to its light specific gravity it accomplishes this very well when added in even as small a quantity as 10 per cent. It is also very nearly pure.

The question comes up occasionally as to whether silica will hydrate when heated and thrown into water. This question must forever be settled by the fact that the analyses of silica treated in such a manner show it to contain 99 per cent SiO_2. If any hydration took place it would be evident in the quantitative analysis. There can be no doubt that the silicas obtained on the market which are washed and treated are therefore pure SiO_2. The silicas made from infusorial earth contain a varying percentage of moisture but the balance is almost pure silica.

China Clay

Synonym, Kaolin; Chemical Formula, $2\,SiO_2Al_2O_3 + H_2O$.

China clay is a white impalpable powder, having a specific gravity ranging from 2.1 to 2.4 and forming a very soft and unctuous product when used in mixed paint. Large quantities are imported into the United States, but the likelihood is that the principal use for clay is either as kaolin for pottery work or as a filler for paper. Still a great many paint manufacturers consider it of use in paint-making. It is not easily affected by acids or alkalis and

very frequently is found in mixed paints as an added filler or as a base in some of the lakes. The percentage of combined water and moisture which it contains will sometimes be as much as 20 per cent of the silicate of alumina. It is not as good for general purposes as some of the other fillers, for the reason that it is certain to separate from the oil and produce a condition on upright surfaces known as "running," and yet it prevents the running or sagging of red lead, even though it produces it with red oxides of iron. Where silicate of alumina is found in a paint made of ochre, the chemist, of course, cannot report the paint as containing clay, because the silicate of alumina of ochre, which will be described later, is a part of the composition of ochre. Sometimes a paint which has a tendency to dry coarse is improved by the addition of clay.

CHAPTER VIII

Barium and Calcium Salts

Barium Sulphate

Synonym: Blanc Fixe′, Lake Base, Permanent White,
Specific Gravity, 2.4.

When a solution of chloride of barium is mixed with a solution of sulphate of soda, a heavy white precipitate is formed which is known as artificial barium sulphate. In all of its chemical qualities it is identical with the barytes of nature, but in its physical qualities it is totally different. Depending somewhat on the method of its manufacture, the grain is exceedingly fine. It has for years been used for the surface coating of paper, because when properly calendered it gives a very high polish and a permanent white surface. Originally it was a French product, the word "Blanc Fixe′" meaning "permanent white." In the early days of the paper industry various compounds of bismuth were used for coating the paper. There are still visiting cards in existence which were surface-coated by means of bismuth carbonate and bismuth subnitrate. These cards were readily affected by sulphur gases, and when it was found that precipitated barium sulphate produced an equally high glaze and the surface retained its pristine whiteness the name "Blanc Fixe′" was universally adopted for the new product.

In the paint industry it was recognized that precipitated

barium sulphate was a valuable adjunct in the manufacture of paint, owing to the fineness of the grain and other phsyical characteristics of the material. It was found, however, that when it was dried and powdered it had lost its extreme fineness and did not mix readily with oil paints. In 1895 Mr. Henry M. Toch succeeded in making Blanc Fixe', which, when dry, was a soft impalpable powder of great value as a base upon which to precipitate lakes, and likewise, when used in mixed paints and enamels, imparted to them, under proper conditions, a vitreous surface which improved their wearing quality. To this product the name of Lake Base was given. A great many paint and chemical concerns have succeeded since then in producing Lake Base of a soft fine texture, and it has become one of the established bases of the paint trade. Its intrinsic value, when properly made, is about equal to that of American zinc oxide, but a number of writers have erroneously stated that its body and covering capacity was equal to zinc oxide, but this statement is not correct. Lake Base is successfully used up to 70 per cent in white pigments, and in colored pigments up to 95 per cent. It is amorphous under the microscope, and is used to a great extent to increase the spreading of weaker or coarser colors.

Barytes

Formula, $BaSO_4$; SpecificGravity, 4.5.

Barytes is a white mineral having the same chemical composition as precipitated barium sulphate. In the United States Geological Survey Reports for 1904, the following statement occurs: "The value of barytes as a white pigment is being recognized more and more each year, and although very little, if any, is used alone for this purpose, it is used

in large quantities in combination with white lead, zinc white, or a combination of both of these white pigments. This addition is not considered an adulteration, as was the case a few years ago, for it is now appreciated that the addition of barytes makes a white pigment more permanent, less likely to be attacked by acids, and freer from discoloration than when white lead is used alone. It is also believed that barytes gives greater body to the paint and makes it more resistant to the influences of the weather. As is well known, pure white lead when remaining in the shade or in a dark place becomes discolored, turning yellowish, while mixtures of white lead and zinc white, or white lead and barytes, or white lead, zinc white, and barytes, retain their color permanently even in dark places."

The amount of barytes that can be mixed with colored pigments without injuring them is remarkably large. There are hundreds of brands of para-red paints made and consumed every year by the agricultural implement trade which contain as high as 90 per cent of natural barytes. When it is taken into consideration that these extremely diluted para-reds cover well and serve their purpose most admirably, the expert should be very careful not to condemn barytes when used in large quantities, for this remarkable behavior is repeated with a large number of other pigments.

No paint chemist will dispute the fact that barytes adds wearing quality to paint, but inasmuch as white lead has set the standard for ease of working, it is admitted that all the other pigments and fillers are not as unctuous as white lead. Therefore the house painter will notice that the so-called lead combination, which contains large quantities of barytes, does not work as freely under the brush as white lead; nevertheless, this objection does not hold good when the

barytes is used in moderate quantities, that is not to exceed one third of the total pigment of a paint. An experiment was made with a mixture of one third carbonate of lead, one third zinc oxide, and one third barytes on an exposed wall of a high building in New York City, in 1885. This surface is still in a moderately good state of preservation, and as a comparison a wall painted five years ago with the pure Dutch process white lead shows that the Dutch process white lead has not stood as well in five years as the combination mixture has stood for twenty years. It is conceded that no paint is supposed to last twenty years, but as a matter of record it is interesting to note that the inert filler added so much to the life of the paint which contained it. In view of this fact, the paint manufacturer is justified in recommending to his customers the use of inert fillers in his paint on the ground of increased longevity.

One hundred pounds of barytes will yield two and three-quarters gallons of paint. Owing to its crystalline structure and specific gravity, it is a more expensive pigment to use than many others when sold by volume, and a paint manufacturer who uses barytes in a mixed paint, and thinks he is the financial gainer thereby, is very much mistaken, owing to the small volume which barytes occupies in a mixed paint. It is also interesting to note from an experimental standpoint that if barytes be mixed with linseed oil and turpentine in the proportion of two pounds to a gallon it will be found that, on allowing these two pounds to settle in a glass jar where it can be observed, it occupies only four per cent of the bulk. In spite of much that may be said in favor of barytes, it is not better than some of the forms of calcium carbonate and some of the forms of silica. As an inert extender silica has advantages over barytes; namely, that while it produces the

same physical effects with equal wearing quality, its cost is lower and it produces a surface for repainting, having what is technically known as "tooth."

The chemical composition of American mineral barytes is different from that of the German. The barytes from Germany will run from 96 to 98 per cent $BaSO_4$. The American barytes all contain larger percentages of calcium carbonate and silica. Those that contain iron are usually bleached by the sulphuric acid process. In 1904 the amount of barytes mined in the United States was about 66,000 tons, and the amount imported, principally from Germany, was nearly 13,000 tons.

Calcium Carbonate

Formula, $CaCO_3$.

Synonyms: Whiting, Paris White, Chalk, White Mineral Primer, Marble Dust and Spanish White.

Whiting is prepared from the natural chalk deposits of the cliffs in the south of England, and Paris White, Extra Gilders White, and Spanish White, are all different qualities of whiting, depending on the amount of levigation and fineness of grain. The mode of preparation is very simple. It consists in grinding the cliff stone in water, washing it, and allowing it to settle in large vats. The cream, or that which is nearest the surface, is dried over steampipes, bolted, and sold as Paris White. The next layers are sold under the name of Extra Gilders White, and the bottom layer as Commercial White, of which putty is made. Whiting is a neutral calcium carbonate, and with the exception of the small percentage of water, which is very variable and depends upon how thoroughly it has been dried, it is remarkably pure and fine. The material at the bottom of the

tubs known as Commercial whiting is never used in the manufacture of mixed paint, because it is coarse, contains silica and iron, and, in attempting to grind this grade, the mills are ruined.

There is a great difference of opinion as to the merits of whiting in paint, but it will be conceded by every manufacturer and paint chemist that the addition of calcium carbonate in some form or other is of great benefit to mixed paint. Some manufacturers put 5 per cent in all the paint they make, excepting that which is made according to specification, for the excellent reason that any acid which may either develop in the paint or be a part of the chemical composition of the paint is slowly neutralized. For paints intended for the protection of metal this practice is to be highly recommended. On the other hand, some writers, who, however, have had little or no practical experience condemn calcium carbonate in any form because it lacks covering capacity or hiding power. If a paint were made of 100 per cent calcium carbonate this statement would hold true, but where other solid pigments are added the argument against whiting fails. No particular evidence need be brought to bear to prove the durability of whiting, for the reason that all putty is made of whiting and oil, and there are buildings and farmhouses in any number still existing where the putty after being exposed to the elements anywhere from twenty-five to seventy-five years is, if anything, better at the end of that period than one month after it was applied. Whiting has the added advantage of being bulky, and priming coats in which it is used present a good surface for repainting. The amount that can be used as an assistant to mixed paint is very variable, depending largely on the pigments or shade which is made. Where a paint is

to be made for the interior of a building in which acid fumes are generated whiting should, of course, be omitted. But there are so many excellent fillers that the use of a single one is not always necessary. Whiting as it is made to-day is never alkaline, for in the drying process it is placed on steampipes and the temperature is so low that dissociation cannot take place.

The other forms of calcium carbonate which are in use are produced by grinding white marble very fine and, generally speaking, these varieties are better for mixed paint purposes than the whiting made from chalk. In the first place, the ground marble or limestone contains little or no moisture; in the second place, they are ground exceedingly fine, and being angular or crystalline in shape they form a better surface if anything for repainting than whiting; and third, where an absolute chemical composition is wanted they produce more uniform chemical compounds. The bulk of both whiting and white filler compounds ranges between $3\frac{3}{4}$ and $4\frac{3}{4}$ gallons per hundred pounds of dry unit.

There is still another grade of calcium carbonate which occasionally appears on the market and is a by-product principally from soap works. It has all the physical characteristics of a good article, but its chemical characteristics condemn it at once as a paint material on account of the free lime which it contains. It is worthless for the purpose of making putty and useless as a paint filler. When putty is made of it it becomes exceedingly hard in the package, and when mixed paint is made of it it forms a lime soap and gelatinizes the contents of the package.

Gypsum

$CaSO_4 + 2\ H_2O$

As an inert pigment or filler gypsum is very largely used in the United States. It is found in twelve states and in very large quantities in Canada. Its specific gravity is 2.5 and its formula as cited above is $CaSO_4$ plus $2H_2O$. This formula represents the gypsum of commerce as sold to the paint trade so closely that the percentage of water in several samples averaged over nineteen, whereas the theoretical is 20.9.

There is a great difference of opinion as to the merits of gypsum as a paint filler, for it must be borne in mind that if it contains any free lime, or if it is not fully hydrated, the lime will act injuriously on the paint and thicken it unduly. The defect produced by its incomplete hydration will be to take up moisture from other materials in the paint so that a hardening or setting process goes slowly on.

Some of the gypsum sold in the east is made from alabaster, this being a native calcium sulphate and is translucent. The Pennsylvania Railroad in its freight car color permits the use of 70 per cent of gypsum, and as good results have been obtained by this company in the use of calcium sulphate as a filler, the condemnation of the material is without much foundation. Due consideration must be given to the fact that thousands of tons of Venetian red are consumed by the paint industry every year, and the composition of Venetian red will average from 15 to 40 per cent ferric oxide, the balance being entirely gypsum. It is nevertheless true that as one part of gypsum is soluble in five hundred parts of water, excessive rainfall will erode it as a paint pigment, particularly where the binder is easily attacked.

COMPOSITION OF VARIOUS SAMPLES OF GYPSUM

CALCIUM SULPHATE	WATER	PERCENTAGE OF GYPSUM	AUTHORITY
77.45	20.14	94.09	Conn. Exper. Station
77.79	21.39	97.59	Orton, Ohio Survey
78.44	20.76	99.18	David T. Day
77.46	20.46	99.20	G. E. Patrick
79.30	18.84	97.92	E. H. S. Bailey
64.63	18.75	98.14	E. H. S. Bailey
67.91	17.72	83.38	E. H. S. Bailey
71.70	18.68	85.63	E. H. S. Bailey
59.46	16.59	90.38	Okarche Cement Co.
69.92	18.85	76.05	E. H. S. Bailey
69.26	21.50	88.77	Paul Wilkinson
64.22	14.00	90.76	U. S. Geo. Survey
....	....	78.22	Wilbur G. Knight
....	....	88.80	Calif. Exper. Station
76.02	19.00	72.60	Calif. Exper. Station
77.76	20.28	95.02	G. P. Grimsley
....	....	98.04	G. P. Grimsley
76.44	20.02	94.84	Conn. Exper. Station
78.60	20.31	96.46	Conn. Exper. Station
....	....	98.91	G. P. Grimsley

CHAPTER IX

Mixed Paints

We have seen from the foregoing chapters the machinery necessary for the manufacture of mixed paints and the raw materials most generally used.

Of all the shades of mixed paints made, the white paints are the weakest and perish the most quickly, and the black paints, particularly those high in carbon and the ferric oxides, are those which last the longest. It is, for instance, impossible to state which of the white paints is the best, and individual opinions or single instances are not permissible for comparison. A test of white lead at the seashore will show that white lead is not as good as other white pigments, and at the same time, in a test in the interior of the country or where climatic changes are not generally marked, white lead will show up wonderfully well. As an instance of this, it may be cited that the United States Light House Department ordered their white mixed paint to be composed of 75 per cent zinc oxide and 25 per cent white lead, for at the seashore this mixture is better than either pigment alone.

A series of experiments conducted by the author showed that white lead perishes through the action of carbon dioxide in rain water. As soon as a film of oil becomes vulnerable the white lead becomes soluble in the rain water, the so-called chalking being traceable to this cause.

Zinc oxide is also attacked by carbon dioxide, but not nearly as quickly as white lead. Sublimed white lead is attacked still less than zinc oxide and zinc lead. The Western zincs and leaded zincs, which vary in their proportion of lead sulphate, are slightly more permanent than zinc oxide, but the moment an inert filler such as barium sulphate, either precipitated or natural, silica and magnesium silicate, are added to the white lead and zinc oxide paints, their resistance to atmospheric influence is largely increased, and therefore these inert materials are an improvement to paint, and where no specification is to be followed they cannot be regarded as adulterants. The principal reason why these inert fillers are not added in greater quantities to white paints is due to the fact that the consuming public is not yet sufficiently educated to the use of these materials. Lithopone has proved itself an extremely valuable pigment, particularly for floor paints, and for marine paints, where shades other than white are demanded, and in no sense can the 70 per cent barium sulphate which is contained in lithopone be regarded as an adulterant, because it is a constituent of the paint itself.

The carbon and graphite paints have wonderful powers of resistance, provided they are properly diluted with a heavier pigment so that the film is thicker. The average graphite paint will cover one thousand square feet to the gallon, but the film produced is so thin that when it once starts to go, either through the abrasive influence of the solid contents of the atmosphere or the decomposing action of water, the surface is soon exposed; but when many successive coats are applied to produce a sufficient thickness, far better results are obtained.

The ferric oxide paints strike a happy medium for they

cover from four to six hundred square feet to the gallon, but their color is limited to three shades — red, brown, and black. As priming and second coats they are, however, ideal, and as finishing coats where these shades are admissible they serve their purpose exceedingly well.

No single pigment is as good as a mixture of pigments, and the intelligent combination of the raw materials always produces the best results.

PAINT VEHICLES

CHAPTER X

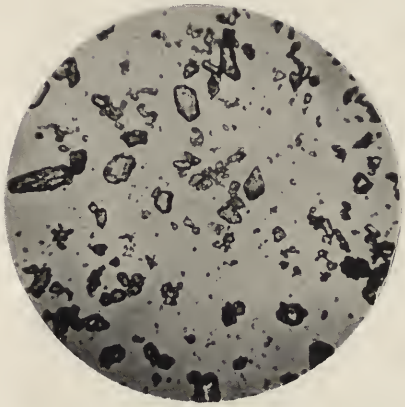
Linseed Oil and Fish Oil

Linseed Oil

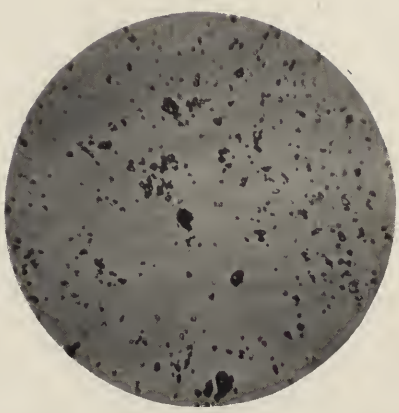
The literature of linseed oil is very extensive. Those who are interested in the theory and history of its use are referred to Mulder, Hooker, Livache, Andes, Hurst, Church, McIllhenny and Lewkowitsch. This chapter will be confined principally to the chemical technology of the oil.

The raw linseed oil produced in the United States comes principally from the northwest. The foreign oils come from Calcutta, the Baltic, and the Argentine regions. There is considerable difference between these oils, the Baltic being perhaps the best and is very highly prized by varnish makers.

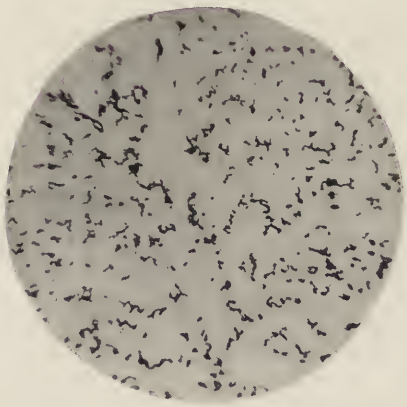
The constants of linseed oil show very wide variations; for instance, its specific gravity will run from 0.931 to 0.935. Its iodine value will vary from 160 to 195 or more, the saponification value being about the same as the iodine value, but running slightly higher. The greatest differences are found in North American linseed oil, the figures being sometimes so perplexing that it is difficult to reconcile them with the standards of Baltic oil. These discrepancies are easily traceable to the natural impurities found in American linseed oil, as, for instance, oils from weeds growing in the flax fields. American linseed oil is likewise inclined to show



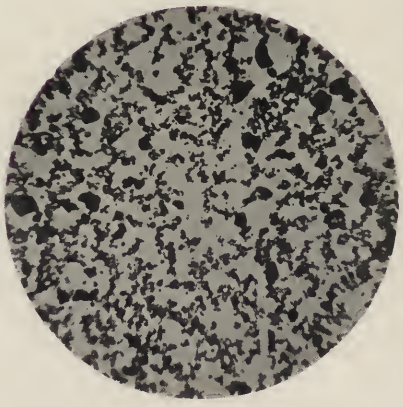
No. 29. American Terra Alba — Photomicrograph X250, very finely powdered.



No. 30. Silica or Silex — Photomicrograph X250, very fine grain.



No. 31. Indian Red — Photomicrograph X300, 98 per cent FE_2O_3, very fine uniform grain.



No. 32. Drop Black — Photomicrograph X300, very finely powdered.

the presence of water to a greater extent than foreign oils, but this, however, is a question of age. If raw linseed oil is allowed to settle until it becomes perfectly clear and shows no sediment or turbidity at 0° C., it cannot be said to contain water. The question here naturally arises as to the use of the term "pure." Calcutta and the Baltic seed are freer from foreign seeds than the American product, and although the amount of foreign seeds which appear as weeds in the field is very small, their presence alters the chemical and physical characteristics of the American oil. Taking Baltic as a standard, it could be reasonably argued that American linseed oil is adulterated, yet no man would have a moral or legal right to condemn American linseed oil because it differed from the Baltic. On the other hand, both climate and soil have a well-known influence on vegetation; even the percentage of oil derived from a given seed cannot be said to be constant. It is also stated that virgin soil produces better seed than a replanted field and this statement appears reasonable.

To how great an extent the natural or negligible admixture of the oil from foreign seeds to linseed oil affects the wearing quality of the oil, it is impossible to say, but it must be admitted that an oil containing up to 3 or 4 per cent of the oil of foreign seeds or weeds will not act as well in the kettle for varnish or boiling purposes as a purer oil. Taking these facts into consideration, a chemist must beware of giving an opinion as to the quality of linseed oil, and where there is no evidence either chemical or otherwise that the oil has been intentionally diluted with other materials, no adverse opinion should be forthcoming. If the examination of linseed oil shows an appreciable percentage of paraffin oil, it can be positively inferred that no weed growth had

anything to do with this adulterant and the mixture must be regarded as intentional or accidental.

Raw linseed oil is extracted from the seed by the old-fashioned method of grinding the seed, heating it, placing it between plates and then pressing it until the remaining cake contains the least possible quantity of oil. The newer method is a continuous process by which the seed is ground and forced in screw fashion through a tube, the oil oozing slowly through an opening in the bottom of the tube and the cake falling out in the end in flakes. When the seed is fed in this manner without heating, a better quality of oil results. The third method consists in crushing the seed and extracting the oil by means of naphtha. The resulting liquid is evaporated, the naphtha recovered and the oil sold for painting purposes. It appeared, however, that this process, while very profitable for the manufacturer, was not profitable for the consumer, and although it made a very fair paint oil, it was found that for the purpose of coating leather, oil cloth, and window shades, the oil had the unfortunate faculty of soaking through the fabric, and when a piece of goods was rolled up too soon and allowed to stand for the greater part of the year, it was almost impossible at the end of that time to unroll the goods, the whole having become a solid mass. Investigation showed that some of the proteids in soluble form were extracted by the naphtha. This was called "new process oil," and it was generally understood that cake made from new process oil was not as good cattle feed as cake made in the old-fashioned way, probably on account of the removal of part of the proteids.

If linseed oil were uniform, both as to source and nature of seed, a chemical formula could be established for it, but because it is not uniform the acids cannot be given in quan-

titative relation. Linseed oil should give no test for nitrogen, but if it does, the proteids in the seed have been attacked. Probably 95 per cent of all the linseed oil made is sold in the raw state, and strange to say, probably 95 per cent or over of all the linseed oil used is consumed in any other but the raw state. It must not be inferred that all paint manufacturers manipulate or treat their linseed oil by heat and other methods of oxidation, for while many of them claim to do so, not one that the author is acquainted with could afford to handle and manipulate linseed oil. At the same time, raw linseed oil cannot be used for the purpose of making paints unless a drier be added, and from the very moment that the drier, either in the nature of a siccative oil, resin, or Japan, is mixed with the oil, the chemical constants of the oil are altered. The change is an irreversible reaction. As an example, it may be cited that if 90 per cent of linseed oil be mixed with 10 per cent of volatile constituents and Japan driers, the chemist cannot separate the three substances and produce three vials containing raw linseed oil in the state in which it was used, and the drier in an unaltered condition. The volatile solvent, if it be benzine, is the only one of the three that can be recovered in any approach to its original condition.

The literature of raw linseed oil is very incomplete, and more attention should be paid by chemical experts and writers to the subject of identification of linseed oil as it really exists in the paint.

In the chapter on the Analysis of Oils, p. 138, it will be seen that when the iodine number of an oil is 180 the same oil when extracted from mixed paint may show 110 and still be absolutely pure, for the reason that the metallic salts which have been added to the oil in the form of Japan or

other siccatives have in a measure saturated some of the bonds of the linseed oil so that less iodine or bromine is absorbed.

Linseed oil dries by oxidation, and this oxidation is hastened by the addition of bases or salts of lead and manganese. There is no doubt that some of these act catalytically, and there is likewise no question that some of these driers continue to act long after the oil is physically dry. In drying, raw linseed oil is supposed to absorb as much as 18 per cent oxygen, but in actual practice where solid linseed oil is used as an article of commerce it seldom absorbs more than 10 per cent of its original weight. The addition of a drier has much to do with the life of a paint, there being no two driers that act exactly alike. If it is the intention of the paint manufacturer to make a paint that will last the longest, he must study the chemical and physical characteristics of the drier which he uses. Red lead, Pb_3O_4, added to linseed oil at a temperature up to 500° F., will make a very hard drying film which in time becomes exceedingly brittle. This can be very easily demonstrated if the red lead oil be coated on cloth and its effect closely watched. On the other hand, the addition of litharge to linseed oil produces the opposite effect and an exceedingly elastic film is produced. The various manganese salts all act differently and are frequently used to excess. Manganese starts the drying operation, the lead salts continue it, and the manganese again hastens the end. Borate of manganese is, perhaps, the least objectionable of all manganese salts, but the black oxide or peroxide is most largely used, and if not used in excess is an exceedingly valuable assistant in the drying of linseed oil.

These driers are usually prepared by adding the oxides

of lead and manganese to melted rosin. After a resinate of lead and manganese is produced, a small quantity of linseed oil is added and the mixture then cooled either with turpentine or benzine or both. There are hundreds of varieties of the so-called Japan driers, the best ones containing the minimum amount of rosin and a certain percentage of the dust of Kauri Gum. The oil driers are made in a similar way, excepting that no rosin is used, and these driers do the least harm. Lime is very frequently used in addition to oil, sometimes in conjunction with rosin and sometimes alone, in order to produce a drying effect. The so-called lime oil will dry with a hard and brittle film. The salts of lead and manganese are not as good for mixed paint purposes as they are for technical purposes. The chloride of manganese when added to linseed oil reacts upon it, and in the presence of any moisture in the oil will liberate traces of hydrochloric acid. Sulphate of manganese and lead acetate will do the same, and wherever there is a trace of liberated acid in paints, their rapid and uniform drying is interfered with. Zinc sulphate and lead sulphate are also excellent driers. It is considered good practice to add a small amount of calcium carbonate wherever these driers are used, in order to neutralize the acidity, and when this is done no ill effect can be observed. Probably the most flexible drier is Prussian blue, which is soluble in linseed oil at 500° F. and produces such a flexible film that the patent leather industry is based upon it.

Some fifteen years ago the author manufactured a new drier which is an improvement on Prussian blue. Briefly described, this drier is made out of a by-product Prussian blue which is treated with an alkali in the presence of calcium oxide and water. A brown powder is the result,

which has no uniformity of color but has given excellent results as a drier. This brown has been erroneously called "Japanners Brown," or Japanese brown. It is soluble in linseed oil at 500° F. and produces a film which is neither too hard nor too soft but remarkably elastic, and admirably adapted for making certain paints and varnishes. It cannot, however, be said to replace any of the good linseed oil driers for mixed paints, as too flexible a paint is not desirable, particularly on steel work or exterior wood work, as blisters are likely to result from the difference in expansion. However, for a base for the manufacture of enamel varnishes and oils this drier has proved itself admirably adapted.

Linseed oil is a glyceride of several fatty acids, and Lewkowitsch has proved that water will replace the glyceride radical and hydrolize the oil. (See Toch on the "Cause of Rust in the Subway," Journal Society Chemical Industry, No. 10, Vol. XXIV.)

The action between a fat and a caustic alkali in boiling solution, by which a soap is formed and glycerine set free, is too well known to need further discussion. The fatty acids which are combined with the soda can be liberated by the addition of almost any mineral acid to the soap. This saponification can be produced by the action of water alone on raw linseed oil. Where a paint contains lime or lead it is probable that this hydrolysis is hastened.

We have here an excellent explanation of the so-called porous qualities, or non-waterproof qualities, of linseed oil as a paint, which is further brought out by the fact that when linseed oil is treated with Prussian blue or Japanners brown it cannot be hydrolized by means of water, for the acid radical has formed a complete compound with the iron in both of these driers and the prolonged heating has

volatilized the glycerine. Consequently, when a paint is made by the treatment of linseed oil at a temperature of over 500° F., with a neutral and soluble base like the ferro-ferri cyanide of iron, the resulting film is not linseed oil nor a linolate of any base with free glycerine, but a complex compound composed of the various linseed oil acids united with iron. This gives us the basis of waterproof paints. This is evident from the quality of patent leather, which is not only much more flexible than any paint made in the ordinary way, but is likewise waterproof.

The following are the probable formulas for linseed oil in its various stages:

$$C_3H_5\left\{\begin{matrix}C_{16}H_{26}O_2\\C_{16}H_{28}O_2\\C_{18}H_{32}O_2\end{matrix}\right\}\text{ Raw linseed oil.}$$

$$\begin{matrix}Pb\\C_3H_5\\Mn\end{matrix}\left\{\begin{matrix}C_{16}H_{26}O_2+O_n\\C_{16}H_{28}O_2+O_n\\C_{18}H_{32}O_2+O_n\end{matrix}\right\}\text{ Japan and linseed oil.}$$

$$\begin{matrix}Mn\\Pb\end{matrix}\left\{\begin{matrix}C_{16}H_{26}O_2+O_n\\C_{16}H_{28}O_2+O_n\\C_{18}H_{32}O_2+O_n\end{matrix}\right\}\text{ Boiled or varnish oil.}$$

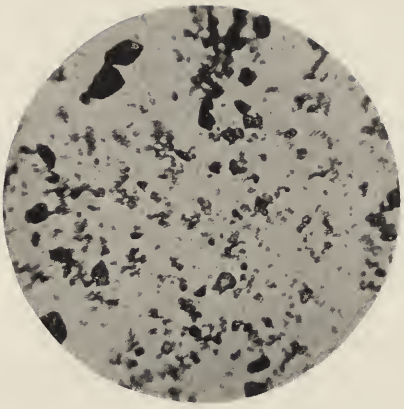
$$Fe\left\{\begin{matrix}C_{16}H_{26}O_2+O_n\\C_{16}H_{28}O_2+O_n\\C_{18}H_{32}O_2+O_n\end{matrix}\right\}\text{ Waterproof oil.}$$

There are questions in regard to the physical and chemical characteristics of linseed oil on which there has been considerable discussion and naturally a difference of opinion. The first is whether linseed oil dries in a porous film, and the second is whether linseed oil while drying goes through a breathing process and absorbs oxygen and gives off carbonic acid and water. With reference to the porosity of

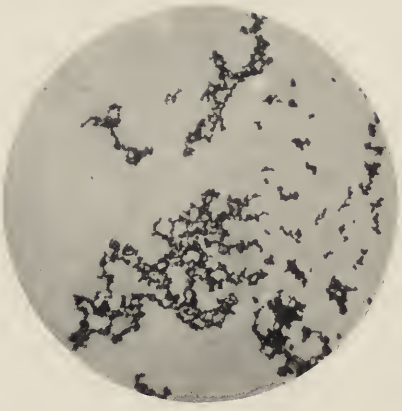
the dry film of linseed oil, the following extract is made from the Journal of the Society of Chemical Industry (May 31, 1905), "New Paint Conditions Existing in the New York Subway:"

"In a paper before the American Chemical Society on March 20, 1903, I gave it as my opinion that a dried film of linseed oil is not porous, excepting for the air bubbles which may be bedded in it, but that any dried film of linseed oil subjected to moisture forms with it a semi-solid solution, and the moisture is carried through the oil onto the surface of the metal. We then have two materials which beyond a doubt have sufficient inherent defects to produce oxidation under the proper conditions, and granted that the percentage of carbon dioxide in the air of the tunnel is not beyond the normal, the fact that carbon dioxide together with moisture would cause this progressive oxidation is sufficient warrant for the discontinuance of paints that are not moisture and gas proof. Dr. Lewkowitsch demonstrated in his Canton lectures that the fats and fatty oils hydrolized with water alone, and linseed oil is hydrolized to a remarkable degree in eight hours when subjected to steam. It can, therefore, be inferred that water would act on linseed oil without the presence of an alkali, and calcium added to water simply hastens the hydrolysis, by acting as a catalyser. This, then, bears out my previous assertion that a film of linseed oil (linoxyn) and water combine to form a semi-solid solution similar in every respect to soap, and inasmuch as we have lime, lead, iron and similar bases present in many paints, it is almost beyond question that these materials aid in the saponification of oil and water."

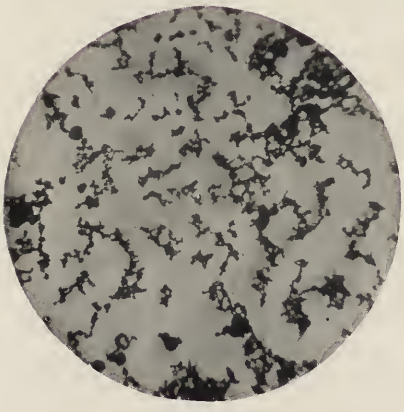
If a drop of linseed oil is spread on a glass slide and one half of it covered with a cover glass, it will be readily



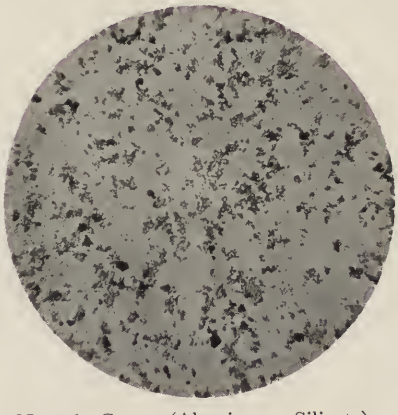
No. 33. Drop Black — Photomicrograph X300, not very uniform.



No. 34. Lampblack — Photomicrograph X300, very uniform.



No. 35. Carbon Black — Photomicrograph X300, very uniform.



No. 36. Clay (Aluminum Silicate) — Photomicrograph X300, very uniform grain.

seen under the microscope that the dried film is as solid as the glass itself; that there are no pores nor any semblance to a reticulated structure visible in the oil; and the author therefore makes the statement with absolute certainty that linseed oil dries with a homogeneous film in all respects similar to a sheet of gelatin or glue.

The question as to whether linseed oil goes through a breathing process, absorbing oxygen and liberating carbon dioxide and water, is one of great importance and one which the author has worked out very carefully with positive results. In the illustration a piece of filter paper two inches in diameter was dipped in linseed oil of known purity and suspended in a flask in air absolutely free from CO_2 and water.

Investigators have always complained of the inability to obtain tight joints in an experiment of this kind, and in order to be certain that there was no leakage, all joints were covered with mercury after having been first shellacked. The manometer gave a curve which indicated the drying, a thermostat being a part of this instrument, so that absolutely uniform conditions were obtained. (See illustration opposite p. 89.) At the end of thirty days the drying curve was obtained, and when the baryta water was led into the bottom of the flask there was hardly a trace of turbidity to be noted. This experiment was repeated many times, always with the same result, and the amount of water or moisture obtained could not be weighed. It was therefore reasonable to conclude that the linseed oil gave off neither CO_2 nor water, but had absorbed oxygen.

The author, however, concluded that this experiment was entirely too delicate, inasmuch as only one gram of linseed oil was absorbed by the paper. Therefore, an apparatus was devised as shown in the illustration, without joints and

so absolutely air tight that the question of leakage could not arise. The flask was filled with linseed oil and then emptied by means of replacing the oil by air free from water and CO_2, and the inside and bottom of the flask were heavily coated with linseed oil which had been previously heated to 400° F. for one hour. The manometer tube formed a part of this apparatus, and when the oil had dried completely (which was manifest by its wrinkled and bleached appearance and likewise by the manometer indication) a rubber tube was attached to the point *E*, a funnel inserted, and a filtered solution of barium hydrate was allowed to run in as soon as the tip *E* was broken. After ninety seconds, the solution of barium hydrate had turned milky, showing conclusively that CO_2 had been generated in the drying of linseed oil.

The next experiments were made quantitatively, and while the amount of moisture could not be accurately measured, the amount of carbon dioxide was in no case higher than $\frac{8}{10}$ of 1 per cent, whereas the absorption of oxygen was 19 per cent. It must therefore be admitted that linseed oil does give off CO_2, but the quantity is relatively so small that it is a question whether it should be taken into account at all.

It is now a known fact that carbon dioxide acts as a rust-producer on iron or steel, and if linseed oil gave off any appreciable quantities of CO_2 and water, they would act as rust-producers in themselves rather than protectors; and while it may be possible that some linseed oils give off more of these two substances than others, the amount under normal conditions cannot be very great, as these experiments show.

Refined or bleached linseed oil is used to a very great

extent for the manufacture of white paints. The methods employed for bleaching linseed oil have not undergone very much change until lately. The coloring matter in linseed oil is largely chlorophyll, the bleaching of linseed oil depending not on the extraction of this chlorophyll but on its change into xantophyll, which is yellow.

Sometimes linseed oil will have a reddish cast instead of the usual greenish cast. This color is attributed to another form of organic matter known as erythrophyll. These three tints, the green, yellow, and red, are analogous to the tints in autumn leaves. All methods for extracting chlorophyll from linseed oil have proved extremely difficult and expensive. The accepted method, therefore, has consisted in the treatment of linseed oil with an acid in order to convert the green coloring matter into the yellow. This is probably the reason why no linseed oil exists which is water white, although the author has made several samples which are almost colorless, but when compared in a four-ounce vial with chemically pure glycerine it can readily be noted how far from colorless the so-called bleached linseed oil is. The method employed for bleaching linseed oil consists in the addition of sulphuric acid and blowing air into the oil at the same time. The oil becomes cloudy and develops small black clots. When this cloudiness is allowed to settle out or the oil is filtered through a filter press, it is very much paler in color and is then known as refined or bleached linseed oil.

Sunlight has a similar effect, the oil produced by bleaching with light and age being superior in quality to thesulphuric acid oil. In the sulphuric acid treatment the oil, the water, and "foots," together with an appreciable amount of emulsified oil, settle to the bottom of the tank. These are drawn

off and are of some value for making cheap barn paints by mixing with lime and the oxides of iron. In another method, which produces a still better bleached oil, chromic acid is used. If a solution of this acid, which is blood red, be added to linseed oil and the mixture agitated, a very much paler and more brilliant oil is obtained, but it is rather expensive to produce. The treatment by means of an electric current in the presence of moisture is likewise used to some extent, but it appears that this method is far more suited to other oils. Great secrecy is maintained among those who have a knowledge on this subject. Peroxide of hydrogen has likewise been recommended, but from the standpoint of cost the sulphuric acid method is still the one that is used to the greatest extent.

The new methods which are favorably spoken of, and which the author has found to be inexpensive and efficient, involve the use of the peroxides of calcium, magnesium, and zinc. These peroxides are made into a paste with water, one pound being sufficient for 200 gallons of linseed oil. This amount of oil is placed in an open kettle or vat, together with the peroxide, and thoroughly agitated. During agitation, a strong solution of sulphuric acid is added which liberates nascent oxygen. If the oil be allowed to settle, or is filtered, and is then heated to drive off any traces of moisture, a very brilliant pale oil is obtained.

It has always been understood that linseed oil contained albuminous matter which coagulated at a temperature of 400° F., or over, and produced a black flocculent mass. When an oil answered this reaction, it was said to break at this low temperature and was useless for making varnish oil and other high grades of linseed oil. G. W. Thompson found that this break was not due to the presence of albu-

minous and nitrogenous matter, but that it was caused by the separation of several phosphates. This explanation has generally been accepted as correct. If an oil, therefore, is allowed to age, these phosphates settle out and the oil does not break. Cold-pressed linseed oil, if it breaks at all, does not break at as low a temperature as hot-pressed oil. Bleached linseed oil does not wear as well as the oil that has been clarified by standing. The demand for brilliant white paints or brilliant enamels is responsible for the manufacture of the so-called water-white oils. From a large variety of tests made by the author it was fully demonstrated that a white paint composed of a mixture of pigments such as sublimed lead, zinc oxide, and white lead all showed absolutely the same whiteness within two weeks after they were exposed to the light, irrespective of the kind of raw linseed oil used. One of the five tests was made with a paint prepared with a linseed oil that had not been aged for more than two months, but within the time mentioned it was just as white as the whitest one of the five.

Linseed oil paints are supposed to deteriorate after a few years and lose their value, owing to the decomposition of linseed oil. This statement is questionable, and while there is no doubt that the ready-mixed paint thickens and changes slightly in its chemical and physical characteristics, the change is exceedingly small in the container which is hermetically sealed. There is no doubt in regard to the reaction which takes place between the oil and white lead, zinc oxide, and a number of the unstable compounds in a mixed paint. While these reactions are very slow, they are at the same time very definite. If the value of a paint were reduced to a curve it would probably be found that the curve would be represented by the arc of a large circle approaching a straight

line. As far as paste paints are concerned, particularly white lead, all painters prize white lead more highly when it is old than when it is fresh.

Fish Oil

The fish oil used for paint purposes is the variety obtained from the Menhaden fish, and when refined by the simple process of filtering through infusorial earth and charcoal, its color is that of refined linseed oil. In its chemical properties it is so similar to linseed oil that it is difficult to differentiate between them. It must be observed that oils in mixed paints are not presented to the chemist or practical man in their raw or natural state, but they have been boiled with driers and ground with pigments so that their characteristics are entirely altered. The old-time painter when he condemned a mixed paint would smell it, taste it, rub it between his thumb and forefinger, smell it again, look wise and say despairingly "Fish Oil." As a matter of fact, the adulteration of paints was seldom, if ever, caused by the addition of fish oil, for the reason that the price of a good fish oil always approximated that of a raw linseed oil, and there were so many other cheaper paraffin oils to be had that the occurrence of fish oil in a mixed paint was relatively rare. Its specific gravity is from .930 to .932. Its iodine number is so close to that of linseed oil that in its raw state, excepting for its characteristic odor and the Maumene test, it is almost impossible to differentiate these oils with a certainty. If a linseed oil be heated to 500°, mixed with Japanners brown or Prussian blue, it develops acrolein, which is identical in odor with that from the fish oil. When Menhaden oil is treated with eight ounces of litharge to the gallon and kept at a temperature of 400°

to 500° F. for ten hours, it thickens perceptibly and can be reduced proportionately with naphtha, but the amount of loss by this treatment with litharge makes it very expensive in the end.

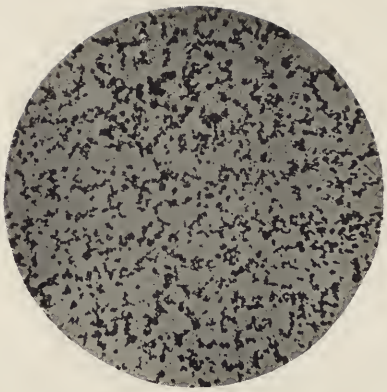
Menhaden oil is the only oil, with the possible exception of China wood oil, which can be used for making smoke-stack paints that will withstand the action of excessive heat and light. When treated as described, its intrinsic value is far beyond that of linseed oil, and a smoke-stack paint made in this manner sells for one third more than a linseed oil paint. It is impossible, however, to treat Menhaden oil for this purpose, except at an excessive cost, because the acrolein developed nauseates the workmen; the loss in evaporation is very large, and the treatment with litharge is such that the oil must be thinned before it has an opportunity to compound or semi-solidify. In its raw state, after treatment with animal charcoal and infusorial earth, it is used to some extent with a heavy boiled linseed oil for making waterproof roof paints, for painting canvas, freight cars, ship decks, etc. When mixed with linseed oil up to about 25 per cent it is extremely difficult to determine the amount present by means of its chemical contents. The characteristic odor known as the "fishy odor" can be relied upon under all circumstances.

The following are the constants of the Menhaden oil which is generally used in the United States for making heat-resisting paints:

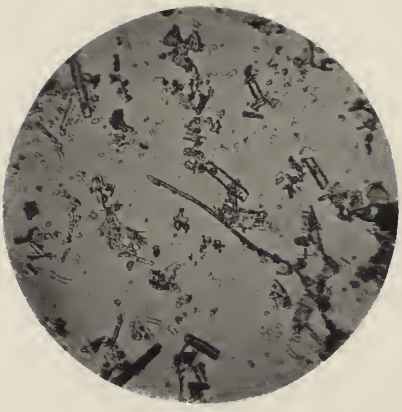
Constants of Fish Oil

Specific Gravity	0.931
Saponification	190.
Iodine Value	150-165

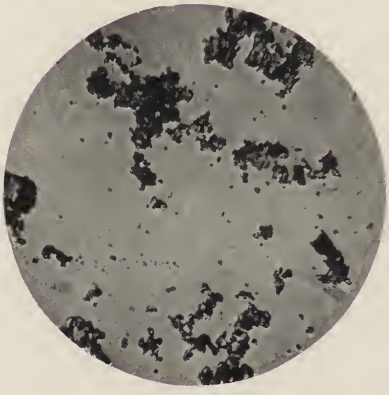
In Newfoundland cod liver oil is used for the same purpose and also for mixing with linseed oil for seashore painting. In the United States, cod liver oil would be too expensive as compared with linseed oil.



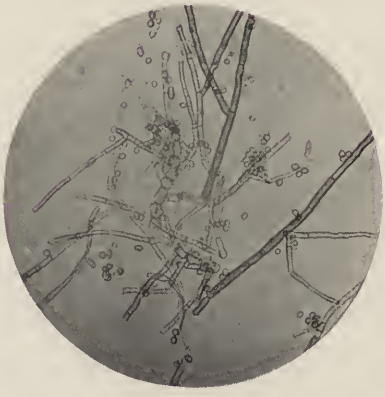
No. 37. WHITING — Photomicrograph X300, very uniform grain.



No. 38. INFUSORIAL EARTH — Photomicrograph X250.



No. 39. TALC (Soapstone) — Photomicrograph X250.



No. 40. CLADOSPORIUM HERBARUM — Photomicrograph X600, a pale fungus growing on damp walls.

CHAPTER XI

CHINESE WOOD OIL

China Wood Oil

Chinese wood oil, or, as it is sometimes known, Japanese wood oil or Tung oil, is very largely used in the United States, but there appears to be very much secrecy with reference to its manipulation.

It is a peculiar fact that the majority of writers on this oil are inclined to condemn it, for the principal reason that when China wood oil, as it is commonly called, is brushed out on a sheet of glass it dries in from thirty to fifty minutes to an opaque film which presents a rough appearance and does not adhere very well to the glass. It is perfectly true that this is a characteristic of China wood oil, and it is likewise true that it has no elasticity and that its waxlike appearance after drying condemns it very thoroughly, but it only goes to prove the difference between theory and practice, for, whereas China wood oil in its raw state is totally unfit for use and spoils any good paint to which it may be added, when properly treated it is one of the most remarkable paint assistants which we have, and those who have studied the subject carefully have made very successful paints.

It might be proper to cite as a parallel case that it would be manifestly unfair to condemn meat as an article of diet for the reason that it is tough, difficult to masticate, insipid

in its taste, and hard to digest. On the other hand, the excellent flavor and nutritious qualities of meat which has been properly cooked and seasoned totally disproves the first statement. It is evidently very unfair to compare raw meat with properly cooked meat.

In the winter time, at ordinary freezing temperature, China wood oil looks like a mixture of tallow and sand and has a similar consistency. The head of the cask is removed and the oil cut out in slices and put into a kettle for treatment.

It is pretty well agreed that at 450° F. China wood oil gelatinizes, and if allowed to cool becomes insoluble. But experts in the manipulation of China wood oil add metallic salts or resinates at this temperature and a small percentage of untreated linseed oil, and before it is sufficiently cool small quantities of naphtha and benzol are added. The resulting liquid is a clear varnish-like oil which dries with a hard elastic film, much more slowly than the original China wood oil. In this condition it possesses most remarkable qualities.

By the use of China wood oil paints are made which dry in damp atmospheres. The advantage which the Chinese and Japanese have had over the Europeans on this subject has been recognized for a long time. It is now known to have been due to their knowledge of the proper manipulation of China wood oil. For the making of marine paints and waterproof paints China wood oil is indispensable.

In the United States preference is given to two brands of China wood oil; one is called the Hankow and the other the Canton, the Hankow being the better of the two. The Canton oil is darker, and it is very likely that it is expressed from the seed by a hot process, whereas the Hankow oil is

expressed by the cold process. The chemical constants of China wood oil are about the same as those of linseed oil, its specific gravity being slightly higher in the third decimal, its iodine value slightly lower, and its saponification number almost the same. The oil has, however, a characteristic odor which cannot be easily destroyed, and a paint manufacturer who is once familiar with this odor can never be deceived. At the same time, where a small quantity of China wood oil is used for the purpose of making a particular kind of calcium oleate, it loses its characteristic odor. The calcium oleate so obtained is eventually split up by atmospheric moisture, and is therefore valuable for making a cement paint which has been patented.

CONSTANTS OF CHINA WOOD OIL AS COMPARED WITH LINSEED OIL

Specific gravity China wood oil	0.935–941
Saponification value	155–190
Iodine value	150–165
Specific gravity linseed oil	0.931–935
Saponification value	175–190
Iodine value	170–180

China wood oil is largely used in the making of enamel paints. Such paints give perfect satisfaction, last longer, and wear better than many of the resin varnish enamels. This work does not treat of enamel paints, although these paints could be classed as mixed paints, because they are a mixture of varnish and pigment. As the ratio of the ingredients is totally different from that of oil-mixed paints, the subject of the use of China wood oil in these enamels has no place in this chapter. Where a manufacturer is at liberty to use any material, China wood oil can in no sense be regarded as an adulterant. It is much more expensive than linseed oil and only on one or two occasions has the

price of linseed oil approximated that of China wood oil, but even if the two in their raw state were exactly the same price, China wood oil would be very much dearer eventually on account of the high cost of manipulation. All factory experience indicates that the manipulation of China wood oil increases its value 20 per cent if based on a cost price of 50 cents per gallon, whereas by the same manipulation the price of linseed oil would be increased only 5 per cent.

Tung oil is probably the glyceride of two acids — elæomargaric and oleic, while linseed oil is probably the glyceride of three acids. China wood oil has two peculiar qualities which makes it very valuable for the manufacture of floor paints. The first is, its resistance to moisture, and the second, its extreme hardness so that it does not show scratch marks. For the manufacture of floor paints for railway and steamship use, these two qualities are essential. On the ferry-boats floating in the rivers of the United States it is customary to wash the floors several times a day. A linseed oil paint soon becomes spongy and is destroyed by this treatment. A floor paint composed of a large amount of China wood oil and a small amount of resin does not show a heel mark very readily, which is a decided advantage.

The Japanese are, however, more adept in the manipulation of China wood oil than any other nation. The author has three samples of varnish oil, one of which has almost the consistency and appearance of chemically pure glycerine. It has a faint yellowish tinge, and while it is no better in its physical characteristics than the normally treated China wood oil, it indicates that without destroying any of its good qualities the Japanese can prepare this oil for lacquer and enamel purposes until it is practically water white.

It is a noticeable fact that there has been great secrecy

among the paint and varnish makers on the question of China wood oil, and those who have used it successfully have forged ahead of their competitors. Its moderate use in a waterproof paint or damp-proof paint is of great benefit. Its use as a mixing varnish or combining medium in mixed paints is likewise of great value. In its constants it is analogous to linseed oil, and it always has a most characteristic odor by which it can be invariably distinguished. It is, however, frequently subjected to adulteration with cheaper oils, and one of the first samples the author ever received was shipped from China in a 5-gallon kerosene tin which contained a considerable quantity of kerosene, either accidentally or intentionally. The oil from Canton, according to the experience of the author, is by no means as good as the oil from Hankow, the Hankow oils being paler in color and responding more clearly to the accepted chemical constants. One of the best tests for the determination of the purity of China wood oil is to heat it very slowly in boiling water for an hour; then transfer the test to a naked flame and heat it for twenty minutes to 450° F. Some care must be exercised not to flash the oil nor to char it. It is then allowed to cool, a good method being to place it in cold water for half an hour, after which time the oil must assume the appearance of an almost solid gelatine. The admixture of any adulterant, particularly cottonseed oil, prevents the coagulation or semi-solidification of China wood oil. In order to manipulate China wood oil as a paint, it must be treated with an organic acid salt of lead and manganese which is sold for the purpose. A number of paint manufacturers have treated China wood oil with great success in the following manner: 10 gallons of China wood oil are slowly heated in a copper kettle to 350° F., and ten pounds of this

organic salt are added. When entirely dissolved, which takes but a very short time, 5 gallons of refined linseed oil are slowly stirred in and the whole heated to 400° F. and kept at that temperature for half an hour. The kettle is now withdrawn from the fire, and 2½ gallons of either turpentine or benzine, or a mixture of both, are added. This oil, known as China base oil, is then used in varying proportions in mixed paints for smoke stacks, floor paints, and varnishes, according to the experience or knowledge of the manufacturer.

CHAPTER XII

Turpentine

Turpentine occupies the same relative position among the vehicles of paints and varnishes as white lead does among the pigments. It is impossible to say for how many generations turpentine was the only solvent or diluent known to the paint and varnish industry, and therefore when other solvents were introduced they were looked upon as adulterants. The methods used in the manufacture of turpentine are very well known; the sap of the Georgia pine and two or three other species of pine trees growing in the southern part of the United States is collected and distilled with steam. The distillate is known as turpentine, and that which remains behind in the still is known as rosin (colophony). American turpentine has a very pleasant odor, and from several combustion analyses made by the author, the composition of turpentine taken directly from the barrel as shipped from the South corresponds absolutely with the theoretical formula $C_{10}H_{16}$. Turpentine at this writing is very expensive, being worth exactly twice as much as linseed oil. It has absolutely none of the qualities of a paint preservative, but is used only to increase the spreading power and working quality of paint. Entirely too much stress is laid upon the value of turpentine as a paint vehicle, and the sooner the chemist and the consumer realize that tur-

pentine is simply an auxiliary, the sooner will better substitutes be used.

If the forestry department of this government will not interfere with the destruction of the trees, turpentine will become a chemical curiosity within the lifetime of many of us, unless new trees are planted.

American differs from Russian turpentine in odor and in specific gravity, although in chemical composition they are alike. The specific gravity of American turpentine is about .865 when fresh, but it will rise as high as .90 when old. It is supposed to boil at 350° F., but that also depends very largely on the condition of the turpentine and whether it has been exposed to the air. Turpentine flashes according to the text-books, and according to the majority of specifications that are written, at 105° F. As a matter of fact, its flash point at 60° F. is 98° F. Turpentine evaporates very slowly, and on account of this slow evaporation it is very highly prized as a varnish diluent, but there are paraffin products that have lately been invented that evaporate just as slowly and leave no residue behind. Pure turpentine when poured on a sheet of filter paper should leave absolutely no residue behind, and a drop of water poured on the paper after the turpentine has evaporated must be absorbed as readily as by the paper before it was immersed. In this regard the petroleum naphtha solvents are identical. They will be described in the proper chapter.

For the analysis of a mixed paint, in order to determine whether turpentine is present, a special apparatus has been invented by which the presence of pure turpentine may be determined, both qualitatively and quantitatively. The principle depends upon the rapid oxidation of turpentine by means of nitric acid. Two c.c. of the distillate supposed

to be turpentine are mixed with four c.c. of nitric acid, the mixture being cooled with ice and water so as to prevent its boiling over and catching fire. The turpentine is oxidized and destroyed, while any paraffin compound which may be present floats to the top in quantitative proportion. A blank, however, must be run, for the reason that some turpentines show about 6 per cent of indestructible matter which must be classed as negligible.

Analysis of Turpentine

The following organic analyses of French, American, and wood turpentine show that French turpentine and American turpentine are both represented by the formula $C_{10}H_{16}$, the American turpentine being practically 100 per cent pure. Wood turpentine, however, may be shown to be 97.7 pure, the $2\frac{1}{2}$ per cent of impurities consisting of pyridene bases, formaline, and other wood decomposition products. Since these investigations were made in 1905, samples of wood turpentine have been placed on the market which are so nearly identical with the sap turpentine that it is almost impossible to distinguish them, only an experienced consumer being able to tell the difference, the wood turpentine having a peculiar odor which is lacking in the sap turpentine. No matter how thoroughly a wood turpentine is purified, there is always a smell of sawdust which clings to it and which can be recognized by a person once familiar with the odor. These pure grades of wood turpentine cannot be said to be adulterants of the sap turpentine.

French Turpentine

	First Analysis	*Second Analysis*
Weight of sample	0.2040 grams.	0.1870 grams.
CO_2 obtained	0.6558 grams.	0.6009 grams.
H_2O obtained	0.2161 grams.	0.1980 grams.
Hence, percentage composition,		
Carbon	87.67 per cent.	87.63 per cent.
Hydrogen	11.87 per cent.	11.87 per cent.
Total	99.54 per cent.	99.50 per cent.

American Turpentine

	First Analysis	*Second Analysis*
Weight of sample	0.1777 grams.	0.1828 grams.
CO_2 obtained	0.5714 grams.	0.5878 grams.
H_2O obtained	0.1923 grams.	0.1968 grams.
Hence, percentage composition,		
Carbon	87.70 per cent.	87.69 per cent.
Hydrogen	12.12 per cent.	12.07 per cent.
Total	99.82 per cent.	99.86 per cent.

Wood Turpentine

	First Analysis	*Second Analysis*
Weight of sample	0.1891 grams.	0.1656 grams.
CO_2 obtained	0.5939 grams.	0.5202 grams.
H_2O obtained	0.2042 grams.	0.1785 grams.
Hence, percentage composition,		
Carbon	85.65 per cent.	85.67 per cent.
Hydrogen	12.10 per cent.	12.08 per cent.
Oxygen	2.25 per cent.	2.25 per cent.
Total	100.00 per cent.	100.00 per cent.

In the Journal of the American Chemical Society* for 1904 a very exhaustive treatise is given on Spirits of Turpentine, in which it is demonstrated that the only reliable chemical

*Analysis of Turpentine by Jno. M. McCandless p. 981. 1904.

test for differentiating between wood turpentine and the old spirits is the determination of the iodine absorption number. But even this is now growing to be very unreliable, for the reason that so much care and skill is exercised in the manufacture of wood turpentine that it is almost impossible to distinguish it from the sap turpentine. A great deal has been written on the optical activity of turpentine when observed through the polariscope. The paint chemist, however, cannot point with any degree of certainty to this test, excepting where a coarse mixture of benzine, rosin oil, etc., is made, and up to the present writing very highly refined turpentine and sap turpentines show little or no difference. The admixture of rosin, oil, benzine, benzene, kerosene, and adulterants of that kind are, of course, differentiated with more or less ease.

Wood Turpentine

The turpentine in the United States is held in such strong hands that the price is abnormally high, and within the last five years pine, sawdust, shavings, tree stumps, and old logs have been placed in retorts and distilled in the same manner as the sap of the pine tree. A liquid is obtained which is sold under the name of wood turpentine and is guaranteed by many to be absolutely the same material as that obtained from the sap of the tree. It must be frankly admitted that there are some wood turpentines in the market at this writing which are so similar to the real article that it is almost impossible to differentiate between them. And yet there is always a peculiar distinctive odor to these wood turpentines which does not exist in the pure turpentines. Several organic analyses of this variety of wood turpentine by the author have shown that the for-

mula is not $C_{10}H_{16}$, but that it is a most complex mixture containing more than a trace of pyridene bases, formic acid, formaldehyde, and other products from the destructive distillation of wood. But wood turpentine is being so continually improved that these impurities are being largely removed. For exterior painting, wood turpentine that contains only a trace of these impurities is just as good as the sap turpentine, and for indoor painting it is no better than a number of the petroleum products and costs very much more money. It cannot be said that it has advantages in exterior painting over the benzine products. One reason why it can be used on exterior work and not on interior work is that the disagreeable odor it sometimes gives off becomes obnoxious to those who use it on interior work. The pure grades of wood turpentine cost within 5 cents per gallon of the price of sap turpentine, and judging from the large number of concerns that have sprung up within the last five years for the manufacture of wood turpentine and then slowly disappeared, it is reasonable to infer that the industry is not profitable. There is one chemical difference between wood turpentine and sap turpentine which has been recently observed, namely, the iodine and bromine absorption numbers of the two products. "Gill," in the Journal of the American Chemical Society of 1903, was the first to publish this fact, which shows that sap turpentine is a different substance from wood turpentine.

CHAPTER XIII

BENZINE AND BENZOL

Benzine

The petroleum products are used very largely in the manufacture of all kinds of mixed paints, the principal one used being that known as "Benzine." It belongs to the series of organic compounds having the general formula $C_nH_{2n}+2$. Although it is frequently added to paint in its pure form as a diluent it is just as frequently added in the form of a liquid drier which is a solution of the original thickened drier in benzine.

Within the past ten years benzine has been so made that its odor is not very apparent, and there is much discussion as to whether benzine is a detriment to paint or not. It is hardly necessary to touch upon the moral side of this question. If a man should order a paint made according to a given specification and free from benzine, or to contain only turpentine as a diluent, the addition of benzine would be a palpable fraud. It is, however, unnecessary to discuss this point. The principal questions for discussion are, first, "Is a moderate amount of benzine harmful to paint?" Second, "How much benzine is permissible in paint?"

Answering the second question first, as to how much benzine is permissible in paint, that depends entirely upon

the paint. A thick, viscous, ropy paint which is so difficult to apply that it will not flow evenly is undoubtedly improved by the addition of benzine. It would be just as much improved by the addition of turpentine; perhaps it would be improved most by the addition of kerosene, especially in the case of very quick drying paints, since kerosene evaporates more slowly than either benzine or turpentine. In the case of such dilution theory fails and only practice can dictate how much diluent can be added. In the case of a dipping paint where the even spreading of a linseed oil paint is desirable, and the sudden evaporation of the solvent helps to produce a uniform coat, benzine cannot be replaced by any other solvent.

The argument that is held forth by many, that benzine is of no value in a structural iron paint for the reason that its rapidity of evaporation lowers the dew point, as then moisture is deposited as it evaporates, is a most fallacious argument, although in theory it is correct. Turpentine will do exactly the same thing and so will any other solvent, depending entirely upon the hydroscopic condition of the atmosphere. If painting be done in an atmosphere where the humidity is high and the temperature near the dew point, it is always found that it makes very little difference what solvents are used, the condensation being apparent in any case. The metallic structure itself lowers the dew point so that the painting is being conducted on a film of invisible water, to the detriment of the paint and to the detriment of the metal. On the other hand a series of experiments made on this subject showed that where the dew point and the humidity are high, condensation easily occurs even though the percentage of moisture in the atmosphere is relatively small. (See "Causes of Rust in the Sub-

way," Journal of the Society of Chemical Industry, 1905, No. 10, Vol. 24.) A great advantage is to be obtained by the moderate use of benzine, for in brushing on a quick-drying paint containing benzine the evaporation carries with it much of the moisture in the paint.

The low price of benzine in America offers a great temptation for its unlimited use. In France and Germany, where the petroleum products are more expensive than they are in America, and more particularly in France, benzine is not regarded so much as an adulterant. However, the physical effects of benzine have been so thoroughly overcome since turpentine has reached such an abnormal price, that a number of most excellent brands have been placed on the market as substitutes, all of which are equal in physical characteristics to pure spirits of turpentine. The objection, of course, to kerosene as a diluent in paint is that it may carry a small percentage of paraffin oil that has a tendency to produce a "bloom" on paint and particularly on varnish.

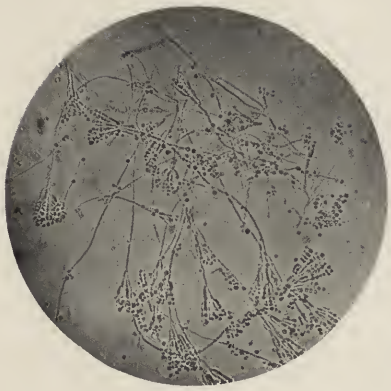
Quite a large number of petroleum products have been placed on the market which are so closely analogous to turpentine that were it not for the odor, or lack of odor, it would be very difficult to differentiate them. As an instance it may be cited that turpentine is a better solvent for some of the mixing varnishes and fossil and semi-fossil resin driers than benzine, but the newer petroleum or paraffin compounds, some of which have had marked success, are absolutely identical in solvent power, speed of evaporation, and viscosity, to turpentine, and while the nitric acid test would clearly show that they are not turpentine, they can by no means be said to be inferior in working quality or solvent power to turpentine. The method by which these benzines are made consists in passing certain paraffin oils

over red-hot coke in conjunction with wood turpentine. The product which is obtained has little or no odor. Thick or viscous paints, particularly the varnish and enamel paints, are so much improved by the addition of these materials that even an inexperienced painter will notice the free-flowing qualities of the material to which these diluents have been added. The petroleum products used in the manufacture of paint are principally 62° benzine, which means benzine having a specific gravity of 62° Baumé. Some of the other naphthas ranging from 71° to 88° are used, but these are so light and bring so much higher price than the 62° that they are not used as much as the 62° naphtha. The newer grades, however, which approach turpentine in physical characteristics, must be counted on as an important factor in paint on account of the extremely high price of turpentine, and the fact that it is strongly held in a few hands. On account of the decreasing amount of this product, substitutes must be recognized. After all, any solvent, whether it be benzine, turpentine, naphtha, benzol or acetone, is nothing but a solvent and evaporates completely, leaving the other vehicles to protect the paint. Of course, too much solvent is a detriment to paint, no matter what kind it may be.

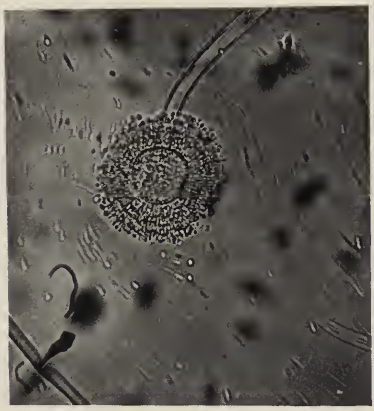
Benzol

This material was for many years known under the name of benzene, and here it must be noted that the benzene which is equivalent to benzol is always spelled *benzene*, and the light naphtha obtained from paraffin crude oil is spelled *benzine*.

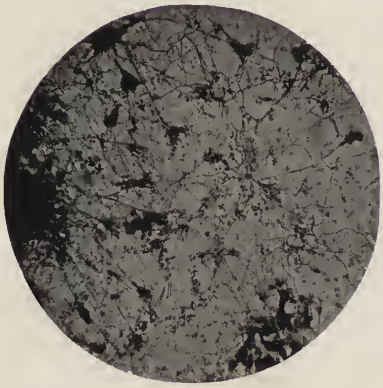
Benzol is the first volatile liquid which is recovered



No. 41. PENICILIUM CRUSTACEUM — Photomicrograph X600, a common green or cellar fungus which grows on many forms of paint.



No. 42. ASPERGILLUS FLAVUS — Photomicrograph X600, yellow fungus frequently found in breweries and dairies, thriving on paint.



No. 43. OLIVE GREEN FUNGUS growing on paint — Photomicrograph X600, PENICILIUM CRUSTACEUM.

No. 44. LITHOPONE (ground in oil) — Photomicrograph X250, exceedingly fine grain.

when coal tar is distilled. It is also sold under the name of solvent naphtha, and in its crude state has a distinctive odor, which for obvious reasons is exactly like illuminating gas. Unlike benzine it has a definite chemical composition represented as C_6H_6. When pure it has an agreeable odor and is such a powerful solvent that it forms one of the principal constituents of many of the paint and varnish removers. It is found frequently in paints for ship bottoms, asphalt, and coal tar paints, and is used to a small extent in the mixing varnishes to prevent their separation. The theoretical chemist will sometimes make a mistake when he finds benzol in a black mixed paint by reporting the presence of coal tar, from the false reasoning that if benzol is present coal tar must be present, because benzol is a constituent of coal tar. A chemist must, therefore, be very careful in drawing such a conclusion, for the presence of either coal or pine tar in a paint can be determined by other methods.

The addition of benzol to mixed paints to be used for priming purposes has been found to be very advantageous, on account of the fact that a firmer bond is formed between a priming coat and the wood, so that when benzol is found in a mixed paint recommended for priming purposes it must be looked upon as a valuable ingredient.

The addition of a very small percentage of benzol to mixed paints does no harm, but if a paint made with benzol and intended as a priming coat be used as a finishing coat it is quite likely to attack the ground coats and produce a shriveled effect.

Driers

Driers for linseed oil paints can be properly divided into two classes:

First — resin driers.

Second — oil driers.

There are probably a hundred or more varieties of each of these two classes, but carefully considered these varieties can be sifted down as belonging to either one of the two just mentioned. The function of a drier in an oil paint is to absorb oxygen rapidly and convert the film into a hard insoluble product, and if the function of the drier would cease when the film is dry, a linseed oil paint would last much longer than it does at present.

Unfortunately all the driers to a greater or less degree continue their action of oxidation so that the paint is eventually destroyed. When we add a drying material to a linseed oil paint the action of natural forces are hastened and the decorative effect is conserved. If we took a pigment and mixed it with raw linseed oil and applied it to a surface, it would take so long to dry that the dust and dirt of the atmosphere would collect on the freshly painted surface, and when the paint eventually did dry it would present a surface most unsightly. We therefore have to add a drying material as being the lesser of two evils, although the driers are in themselves destroyers of paint. That all driers act catalytically, some to a small extent and others entirely, is now admitted as a fact.

Briefly described, oil driers are all composed of linseed oil heated to between five and six hundred degrees with some salt of oxide of lead and manganese until the product thickens. Then it is reduced with benzine or turpentine, or a mixture

of both. This class of driers is known as "oil driers," and by themselves, when spread out in a thin film on glass, remain tacky for a long time. The other form of driers known as the "Japan driers" are metallic salts or bases fused with rosin or resin and linseed oil and reduced with benzine or turpentine. When these Japan driers are spread on glass they dry like a varnish in a short time.

Of the two classes of driers the "oil driers" are the better, their progressive oxidation being slower than that of Japan driers. The paint manufacturer should have some knowledge of the manufacture of driers, for it can be cited as a distinct example that in the making of red lead paints containing a varying proportion of red lead, a Japan drier will form an additional compound with red lead and produce a livery, spongy paint, which unless quickly used becomes totally unfit for use, whereas the diluted oil driers being thoroughly satiated, form no compound with the lead bases and keep red lead in a normal condition longer. It has been argued that the resinates of lead and manganese when properly made should not saponify a red lead paint, but this argument does not hold good, for a resinate of lime, lead, or manganese drier has additional affinity for a lead base, which cannot be said of the oil drier.

CHAPTER XIV

COMBINING MEDIUMS AND WATER

Combining Mediums

In certain classes of mixed paints, particularly house paints which are made of corroded lead, sublimed lead, barium sulphate, etc., there is a likelihood or tendency of the pigment to settle. This is more marked in the case of corroded lead than in any of the other pigments. To prevent this, in a measure, water is added, and up to a certain percentage both the manufacturer and the consumer have accepted the fact that water is not injurious when added up to 2 per cent for the purpose of combining the paint; but beyond this percentage its effect is likely to be injurious.

Sometimes for the sake of an argument, but more often for the sake of making a paint which contains no more water than the natural moisture of its constituents, a manufacturer feels the necessity of adding a combining medium other than water to prevent the paint from settling hard in the package. Among these are gutta-percha solutions, solutions of balata, para-rubber, gum chicle, etc. The rubber solutions mentioned serve their purpose very well without injuring the paint, and the percentage used is so small that it may be considered negligible. This, however, is not true of many of the mixing varnishes which are made by varnish manufacturers who have no experience in the manufacture of paint. They sell rosin varnishes neutralized with lime,

lead, or manganese, and while they assist very well in combining the lead with the oil, the wearing quality of the paint is proportionately reduced.

Within the last few years a new combining medium has appeared on the market which in itself is an improvement on all paints. It is made by melting a mixture of a resin (free from rosin or colophony) and heavy linseed oil and reducing with China wood oil and naphtha. Where a manufacturer uses a combining medium of this character the paint becomes more viscous as it grows older, and when it dries it produces a satin-like gloss and shows fewer brush marks than a paint containing water.

Water in the Composition of Mixed Paints

The question of how much water shall be added to mixed paints, or how much water mixed paints shall contain, either added or incidental, is not fully decided upon, as there is a difference of opinion as to its value, and likewise a difference of opinion as to the amount necessary for certain purposes. There are some paints in which as high as 2 per cent water are necessary, and in other paints less than 1 per cent is purposely added. That water is of great benefit in certain paints cannot be disputed, one large railway corporation permitting the addition of 1 per cent of water to its mixed and paste paints.

A chemist in making an examination of a mixed paint must necessarily be careful in giving an opinion as to the amount of water in the paint, and great judgment must be used in a report. For instance, a paint, made according to a certain specification, containing a large mixture of Venetian red and yellow ochre, might contain very nearly 2 per cent of moisture, which was a part of the composition of the pigment.

Then again, linseed oil frequently contains more than a trace of water, which the manufacturer cannot extract nor can he afford the time necessary to allow the water to settle out of the oil. A mixed paint should not contain over 2 per cent water, for it is unnecessary to add more than this amount to any paint.

The proper benefits derived from the addition of water to a pure linseed oil paint are suspension of the pigment and improvement in its working quality. Take the case of artists' tube colors which lie on the dealers' shelves for years and which are prone to get hard and likely to separate so completely that the color will be found on one side of the tube and the oil be entirely free on the other. Water is an absolute necessity in this case and is an improvement for both seller and user. The colors made with the correct addition of water are known to "pile" and artists prefer a color which "piles" properly.

There are many ways of adding water to a paint. In some instances the required amount of water, together with the oil and the drier, are placed in a churn or mixer and the paste paint stirred in. Where materials like calcium sulphate, calcium carbonate, ochre, Venetian red, silicate of magnesia, silicate of alumina, white lead, etc., are used, there is no necessity for adding any combining material which will form a soap with the linseed oil, there being sufficient action between these materials and the water. It is an additional advantage that there is less likely to be complete saponification in a mixed paint to which no "emulsifier" has been added.

There are a large variety of materials which are used for "emulsifying" paint, some of which are good and some of which tend to gelatinize the paint. The materials used

for "emulsifying" paint are the carbonates of all the alkalis, borax, zinc sulphate, calcium hypochlorite, manganese sulphate, manganese chloride, ferric chloride, lead acetate, ferrous sulphate, alcoholic solutions of these various salts, also the alcoholic solutions of these salts containing a small percentage of moisture.

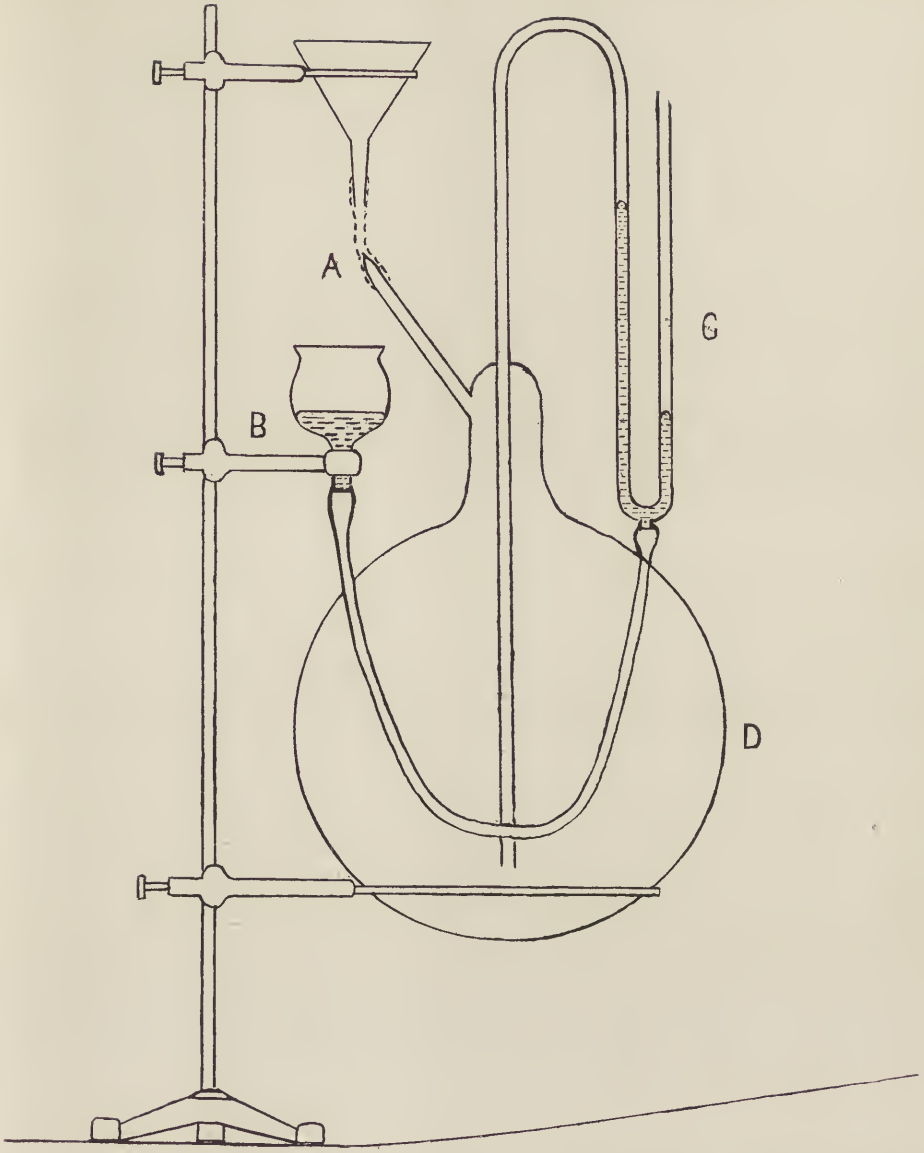
To detect water in paint, particularly in light-colored paints, is a comparatively simple matter. The method devised by the author is almost quantitative for some purposes. The first method ever published by the author consisted in placing a strip of gelatin in a mixed paint. When a measured or weighed amount of mixed paint was taken and the strip of gelatin allowed to remain for twenty-four hours a fairly correct quantitative determination was obtained. Another method described some years ago involved the use of anhydrous sulphate of copper, a bluish white powder which on the addition of water returns to the natural dark blue color of crystallized copper sulphate.

The author has, however, devised the scheme of using a glass plate and mixing a paint with a dyestuff known as "Erythrosine B." When about ½ gram of the dye and 5 grams of mixed paint are rubbed together with a pallet knife on a sheet of glass, a paint containing no water will produce a distinct pearl-gray color; if there is water in the paint the mixture changes almost immediately to a brilliant cerise red, and if there is much water in the paint (over 2 per cent) the color changes into a crimson so that the reaction is clearly marked. The test must not be allowed to stand more than four minutes, since even paints which contain no added water but which naturally contain traces of moisture will begin to change into a rosy color, but this indication points to the absence of water.

In a red, black, or other dark-colored paint where this color reaction cannot be seen, the oil must be separated from the pigment and a test made of the oil on a sheet of milk glass. It is always necessary to run a blank alongside of the test, the blank being of known composition. For instance, in testing a yellow paint composed of ochre, a certain amount of water will be found in the dry color. It is therefore necessary to make a yellow paint containing ochre and test it with Erythrosine and note how long it takes for the water in the ochre to attack the Erythrosine. The suspected sample is then tested, and if it changes in the same time as the known sample no added water can be reported. A white paint very largely composed of moist white lead will show the Erythrosine reaction in a few minutes, and a chemist who has standard samples of known composition at hand will find this test both delicate and useful.

There are a large variety of indicators such as nigrosine black, insoluble in alcohol but soluble in water, which are very useful indeed. Some manufacturers have been known to add a borax solution of rosin and shellac, which contains a small percentage of wood alcohol, to certain paints.

The wood alcohol in this case would give a very brilliant color with the Erythrosine, but the nigrosine being insoluble in alcohol would give its color only with water. I am indebted to Mr. Louis Waldman, president of the Hudson River Aniline Works, for the large and complete number of indicators which he sent me for experimental purposes. The dyes mentioned above can be obtained from the Hudson River Aniline Works or their sale agents in New York, The Continental Color Company.



No. 45. D is a glass flask of about 2 litres capacity. Through the tube A 3.4 grams of refined linseed oil, which had been heated to 400 degrees F. for one hour, were introduced and well distributed over the inner surface of the flask. Dry oxygen free from CO_2 was blown through the flask, by means of tubes A and C, until the flask contained pure oxygen. The tube A was then sealed, as shown in sketch, mercury brought up into the manometer by elevating B to the position shown. The flask was then filled with oxygen at atmospheric pressure and effectually sealed. As drying proceeded and oxygen was absorbed, the diminished pressure was read off on the manometer. When this became constant the funnel which was connected to A by a rubber tube was filled with filtered Barium Hydrate solution, and the point at A broken, allowing this to run into the flask without admission of air. In a few minutes Barium Carbonate was formed, showing conclusively that some CO_2 had been generated by the oil.

CHAPTER XV

SPECIAL PAINTS

Floor Paints

Much space cannot be devoted in this book to *Floor Paints*, for properly speaking they are enamels and not mixed paints. It is quite true that in former years floor paints were good linseed oil paints which dried in from twenty-four to forty-eight hours. The film was never hard, and owing to the large amount of linseed oil used in the manufacture of these paints they wore very badly. The present practice is to combine for floor paints the inert pigments and hard drying varnishes. A floor paint should dry sufficiently hard over night so as to show no scratch or heel mark in the morning. For the lighter shades, including the gray paints, lithopone forms an ideal pigment and China wood oil answers the purpose of a vehicle far better than linseed oil. A resin varnish cooked with China wood oil which has been properly neutralized gives a tough, elastic, and waterproof film on the floor which cannot be obtained by the use of the old-fashioned varnishes, if the time of drying be taken into consideration.

It is becoming the custom to paint cement floors, and while this was regarded as a dangerous proceeding up to within the past year or two, a patent was granted for a cement floor paint which does not attack cement. It is made on the principle that the liberation of calcium hydrate

in concrete is prevented by treating it with an acid resin which forms the neutral resinate of calcium. Engineers have noticed for some time that lubricating oils, particularly those containing fatty acids, destroy cement floors. Linseed oil was regarded as a dangerous factor for the same reason. A crystalline compound of the fatty acid and the lime was formed which expanded the floor surface to such a degree that sometimes the foundations in round houses were destroyed.

Cement Paint

It has been noted for a long time that Portland cement, or its equivalent, is under certain circumstances a permanent protection for steel and iron, but every attempt to make a Portland cement paint by the mixture of Portland cement with any binder, particularly linseed oil varnish, has proved a failure. A successful cement paint has, however, been made under the name of *Tockolith*, the theory of which has been very carefully worked out. Instead of Portland cement, a material composed of 85 per cent of an artificial compound equal to $SiO_2,3CaO$ and 15 per cent of a compound Al_2O_3, $2CaO$ is used. As a material of this description has no covering property or hiding power, and is likewise too pure to be used as a coating, it has been found that when it is diluted with 50 per cent of a pigment it resembles a paint very closely. The binder consists of an oil so treated that glycerine is set free and lime is made to take its place. By a very slow process of setting, the film thus prepared has been found to give most excellent satisfaction. Further details in regard to this material can be found by consulting the Journal of the American Chemical Society, Vol. 25, No. 7, and likewise the patent records.

Perhaps the most peculiar part which this material plays in the protection of steel and iron is shown by the fact that if it is coated over a sheet of steel which has already begun to show a reddish yellow rust of the composition of Fe_2O_3, $2H_2O$ the rust will be absorbed by the cement and a calcium ferrite is formed by interchange. The material Fe_2O_3, $2CaO$, is a material known to exist in ordinary Portland cements. This reaction is certainly very interesting and unquestionably some such reaction must take place, for it has long been noted by engineers that rusty steel embedded in a wet and close concrete comes out almost clean after a lapse of years.

The author cannot go into this subject any more deeply because this discovery is his and he is interested in the manufacture of this material, and this book is not the place to exploit a proprietary article; but inasmuch as this paint has been regarded by many engineers as at least a step toward the solution of the question of the protection of iron and steel, it is fitting that this brief mention of the material should be made.

Damp-Resisting Paints

Paints of this character are comparatively new, the first one having been manufactured by the author's firm and put on the market in 1892. It was made for the purpose of coating brine pipes and other pieces of machinery which were continually under water. The original paints of this character were produced by melting a good grade of asphaltum and adding a sufficient quantity of gutta-percha, together with a suitable solvent and a small percentage of pigment. These paints served their purpose very well and were used

very largely, but no matter how carefully compounded, the gutta-percha separated from the asphalt base if the paints were allowed to stand for any length of time.

Further experiments showed that cement mortar would adhere most firmly to a paint of this kind. The paint could be applied even to a new brick wall, lathing and furring being omitted. It took such a long time, however, to introduce a paint of this character to the building public that the author's firm never thought it worth while to patent the application.

Damp-resisting waterproof paints are now an adopted fixture in the paint industry, and while bitumen forms the base of paints of this character, treated China wood oil, and treated linseed oil in which glycerine is replaced with a suitable metallic base, should be added when making these paints. They are used widely and in various ways, having served their purpose so well that engineers are beginning to adopt paints of this character as priming coats for metallic structures wherever cement or cement mortar is to be applied, so that oxidation by electrolytic action may be prevented.

Paints for Breweries

The Influence of Paint on Malted Liquors

During the year 1905 several breweries suffered great loss through the use of a paint containing tar. The beer which was fermenting at the time of the application of this particular tar paint had absorbed a distinctly tarry odor.

It has long been known that food products lying in cold storage absorb particular odors. It is likewise well known that tobacco is extremely sensitive to certain materials, such,

for instance, as the terpenes, camphor, etc., but brewers had never paid any particular attention to the composition of the paints used in a brewery, and so it occurred that when the walls of several breweries were painted black it developed that the black paint was composed of tar and that the characteristic odor of benzol and cresylic acid was imparted to the beer. The worst feature, however, of the use of an unknown or unreliable composition in a brewery is the impossibility of removing the application from the walls, and a remedy is not always easy to prescribe. Upon thorough investigation of this subject it was found that there were quite a number of substances which had a deleterious influence on malted liquors, either in process of fermentation or in storage. The following experiments have demonstrated that the brew-masters should be very careful and particular in selecting a material for the preservation of the walls.

A black waterproof paint applied to the walls and ceilings of the fermentation rooms is very desirable, for the reason that any mold starting to grow would be at once noticed, because the first growth of a mold such as Mycelium is always white. The appearance of a white fluffy material resembling cotton is readily noticed on a black background. A stream of water from a hose could be applied to the walls from time to time and the atmosphere kept perfectly clean. This plan met with very great success, a number of brewers having adopted this color in painting the ceiling and the walls of the fermentation rooms. A paint of this sort which was free from any noxious material and withstood the dampness of these rooms was necessarily not a cheap concoction but a carefully made compound. There is so much unfortunate competition of the "just-as-good-for-less-money kind" that in some breweries for the sake of a few

dollars a tar paint was substituted for a paint which had answered a good purpose. The damage estimated to have been caused by the tar paint in one brewery was placed at $100,000, whereas the saving in the cost between the two paints would have been perhaps $50. Tar is worth about 20 cents per gallon, and it is a great incentive for a purchasing agent to buy a black paint for 50 cents per gallon when he had previously paid $1.00, for the "just as good" argument is never lacking; but he is not aware that the 50-cent material is only worth 20 cents and under its proper name could be bought at that price.

The worst consequence, however, of the application of the tar paint is, as stated before, the difficulty of painting over it so that the persistent odor of benzol and cresylic acid is not apparent in the brewery. However, two good applications of shellac varnish over the tar will hermetically seal it up. Over this the proper article can then be applied.

A series of experiments were tried with various materials by coating the interior of a tin can having a loose cover, and placing in this vessel a glass of any malted liquor and then replacing the cover. At the end of an hour, the malted liquor being removed, it was found that the odor of the tar paint had been thoroughly absorbed by the beer, which had a faint odor of cresylic acid. The next material which had likewise spoiled the beer was a so-called Banana Liquid, which is a solution of cellulose, or gun cotton, in acetate of amyl, and is commonly known as Banana Liquid. It has become quite a fad to paint steampipes and exposed plumbing pipes with a mixture of this liquid and aluminum bronze. Under ordinary circumstances this makes a very good waterproof coating for such exposed pipes, but in a brewery its use should be absolutely prohibited. While the malted

liquor may not be spoiled or unfit for use through the absorption of the odor of acetate of amyl, a faint aromatic taste, and odor of so-called Pear Oil, which is undesirable, is detected. Wherever aluminum bronze is to be used in a brewery the same purpose is served if the pure aluminum be mixed with a diluted interior spar varnish from which no ill effect is felt.

Another experiment was made with the various grades of paraffin, which in some breweries have taken the place of varnish for coating the interior of the vats. A number of misleading statements have been made in regard to the cost of paraffin compared with other good materials, it having been asserted that paraffin was far cheaper than any material that could be used. In practice, this, however, is found to be an error for the reason that the cost of application of paraffin on account of its high viscosity when melted (which lowers its spreading power), compared with the cost of application of the proper kind of spirit varnish, outweighs the initial saving on paraffin. In addition the paraffin, ranging in melting point from 105 to 125° F., contains volatile oils which in taste and odor resemble kerosene. While it may not be a scientific test it is, however, of great practical value to chew a piece of paraffin in order to determine its taste. About twenty-five years ago paraffin was sold in this country mixed with sugar in small tablets as a chewing gum, but its disagreeable taste even at the temperature of the mouth soon destroyed its sale.

Another material which was formerly used in large quantities in breweries, but the use of which within the past five or six years has been abandoned, is a material made of a high-grade gum dissolved in bisulphide of carbon. It is strange that this ill-smelling material is not absorbed by

beer to any great extent, but it reduced the activities of the workmen and in some instances produced bad effects. There is, however, no need for the use of any such noxious solvent in these days when there are so many good solvents which have no bad effects either on beer or on the workmen.

The so-called cold-water paints have had a great deal to answer for in breweries. There was a time when it appeared as if cold-water paints would supplant many of the better grades of paints entirely. Cold-water paints are made of whiting, asbestine, or some such mineral substances, mixed with caseine and a solvent such as borax or phosphate of soda. Caseine is obtained from milk, being a complex nitrogenous substance almost identical with albumen. As a glue it has exceptional qualities. As a cold-water paint this mixture is used a great deal in loft buildings and other places where it is continually dry. On a cellar wall, or in a brewery, its use should be prohibited for the reason that caseine forms a most excellent nutrient for all fungi, and these fungi are responsible for many foul odors. The fungus known as the Penicilium crustaceum is a pale green fungus which is frequently noticed on cheese. It multiplies very rapidly and gives to a room that peculiar musty odor known as the "cellar odor." There are about eight or ten other fungi which likewise grow on cold-water paints, some of them having little or no odor, while others, particularly the black known as the Aspergillus Niger, are very disagreeable and distasteful. If the cellar wall which is continually damp is to be coated white a good liberal application of slacked lime, together with an inorganic binder, is very desirable and does no harm. When the New York subway was first painted a small section was coated with cold-water paint of the caseine type. It is very fortunate that the ill

No. 46. Determination of CO_2 and H_2O in Drying of Linseed Oil — A piece of filter paper was immersed in pure linseed oil, and, after the absorbed oil was weighed, the filter paper was suspended in the Erlenmeyer flask, on the bottom of which was a solution of Barium Hydrate (free from CO_2) to absorb the CO_2 formed by the drying of the oil. The flask was immersed in a water-thermostat, the water of which was stirred by a revolving mechanical stirrer. A thermo-regulator, by means of which the gas-flame under the thermostat was automatically regulated, was placed under the flask. By opening the glass-cock, oxygen was admitted from time to time to the Erlenmeyer flask, and the absorption of oxygen was read on the mercury-manometer. The readings were always made at the same temperature. The oxygen, before entering the Erlenmeyer flask, was passed through the KOH bulb, where it was washed free from CO_2. This experiment was conducted in triplicate with great care, the joints being all sealed with shellac and placed under mercury. No CO_2 or H_2O beyond a trace could be determined, owing to the small quantity of linseed oil which the filter paper contained.

effects were soon discovered, for had the entire interior been coated with this material it would have been impossible to run trains through it owing to the foul odors which would have been generated. In the newer part of the subway beyond 157th Street a cold-water paint was used on the walls. It contains an inorganic binder known as Germ-Proof paint. This section is remarkably free from odor.

The materials which do not affect malted liquors in any degree are the linseed oil paints, the turpentine varnishes, the benzine and naphtha paints, and the alcohol varnishes. Turpentine is absorbed to a very small degree by malted liquors but without any deleterious effect. Benzine and naphtha, particularly the benzine of 62° gravity, is not absorbed at all, and most gum resins are particularly suited for breweries. The resins which should not be used in any brewery are those of the pine tar variety or of the cold tar and pitch class. The enamels used in breweries for decorative and preservative purposes are nearly all harmless, there being only one harmful sample that ever came to the author's notice, and that contained a small amount of acetate of amyl.

With reference to brewer's varnish, it may be said that within the last five or six years a great deal of attention has been given to the manufacture of this varnish, the general trend among manufacturers being to produce an article of a purer and higher grade than was formerly made. For instance, it was the custom to sell according to price and not according to quality, and shellac was often adulterated with 50 per cent colophony (rosin). Shellac is not attacked by water or wort, but rosin is very easily attacked. Water hydrolizes it and turns it uniformly cream white and soft. In this condition it is known to be a most excellent nutrient

for the second generation yeast, which would not be formed if the varnish were pure. Another material known as iron varnish, which was used for the lacquering of the interior of iron receptacles, has been the subject of much adulteration. In Germany this varnish is known as Eisen Glasure, not because it was used for coating iron but because it contained iron as one of its constituents. Many manufacturers in order to cheapen the product have used low grades of garnet shellac, sapphire variety, etc., in the spirit varnish. It was frequently found that these so-called iron varnishes did not last any length of time at all. A careful analysis of the best iron varnishes demonstrated that they were made of a very high grade of shellac and were originally of a very pale yellow color. The varnish was then taken and an even soluble of alcohol, and the exact amount added necessary to combine with the free tannin of the shellac, and then this was allowed to age for several weeks. It makes a most desirable varnish for the purpose. The shellacs known as garnet are almost all impure, being adulterated before they reach this country.

The brew-master, therefore, will find it to his advantage to investigate very carefully the paints and varnishes which he buys, for an exact knowledge of the nature of the materials to be used will always save much trouble and exert a favorable influence on the resulting product.

CHAPTER XVI

ANALYTICAL

The Analyses of Mixed Paint

The analysis and chemical examination of a mixed paint is by no means a simple matter, and not every chemist is fitted for this work. The intellectual development of a man's reasoning power is of vast importance in all scientific work, but the science of "deduction," if there be such a science, would be of the greatest importance in the training of a chemist. Woe to the chemist who starts on a false premise for he can be misled into most impossible conclusions, and if he be a man of recognized authority in other branches, his mistakes can ofttimes create a great deal of havoc. Reactions in paint chemistry are almost always irreversible, if they be organic. If a mixed paint be made of silica, calcium carbonate, and zinc oxide, it can readily be seen that these pigments can be extracted from the paint and recovered almost exactly as they were put into the mixture. If the vehicle be composed of raw linseed oil, white Japan, turpentine, and benzine, it is impossible to regain these four liquids and separate them into four vessels as they were originally used. The inorganic part of this mixture can, therefore, be determined with great accuracy, but the organic part cannot.

Personal experience, or a knowledge of the experience of

others, is of great assistance in the intelligent examination of a paint, and the surest proof of the correctness of an analysis is to make the synthesis. A chemist who will find benzol (C_6H_6) in a black paint, and who will report by inference that this paint contains coal tar because he found benzol in it and because the paint was black, makes a very serious error. A paint analysis can often be compared to an analysis which the author saw of some biscuit crumbs. The biscuit crumbs were made of flour and water and baked in an oven. The analysis showed starch, potash, silica, and carbon, and no comment need be made on the value of such an analysis. If we take raw linseed oil and manipulate it as shown in the chapter on "linseed oil" so as to free it entirely from its glycerine and form a fatty, acid salt, the chemist will make a serious error if he condemns the fatty acid salt because its constants do not agree with those of raw linseed oil. Nearly all of the organic vehicles used in paints, except the absorbents, undergo a chemical change, and for this purpose careful study is necessary before an opinion is given.

Separation of the Vehicle and Pigment

The simplest method for the separation of the oil from the pigment is to place the paint in a tall beaker, stand it on a sand bath and heat it, covering the top of the beaker with a watch glass to prevent loss by evaporation. As soon as the paint becomes warm the viscosity of the oil is changed, and in the course of an hour or so the pigment separates from the oil, which can be drawn off for examination. There is, however, a large quantity of oil which remains mixed with the pigment. The second operation consists in diluting

the sediment with a mixture of benzine and benzol. The paint is again warmed and the supernatant liquid drawn off. The third washing can now take place with benzine only, leaving the pure pigment. Paints containing an excessive amount of emulsion are, however, difficult to analyze in this way, and in order to obtain a rapid separation of the oil and pigment it is well to make a mixture of pure acetone, 98 per cent wood alcohol and benzol, which will extract the oil and water from the mixed paint. By very careful manipulation freshly distilled wood alcohol or Columbian spirits absolutely free from water, when mixed with an emulsion paint, will extract the water, which can be recognized at once by treating the extract with a crystal of nigrosene V. X., made by the Hudson River Aniline Works, which is not soluble in wood alcohol but soluble in water, producing a purple black ring in the bottom of the test tube.

Graphite Paints

The determination of the percentage of carbon in graphite is best accomplished by heating to redness in a porcelain crucible, a gentle current of oxygen being allowed to flow into the crucible. This insures complete and rapid combustion. There are several simple methods for the detection of graphite in paint.

First. The percentage of pigment in a graphite mixed paint is always very small—under three pounds to the gallon.

Second. If an extracted pigment be rubbed on the palm of the hand it very soon assumes the characteristic appearance of stove polish, which is obtained from no other black pigment. This test although empirical is very reliable, even when there is a small amount of graphite in the black paint.

Red Paints

If a good separation of the pigment from the oil be made, it is comparatively easy to determine the base of the red paint. In a permanent vermilion the pigment should be ignited in a porcelain crucible and the loss noted. Another portion should be extracted with an alcoholic solution of potash until no color remains, and weighed. The loss in weight produced by the alcoholic alkaline extract, plus the loss produced in calcining, gives the amount of dye in the material. The analysis of ferric oxide paints is, of course, quite simple, the usual methods for the determination of iron being reliable. The dry oxide, however, must be carefully washed and an ordinary horseshoe magnet applied to the sample. If the color is red, or a reddish brown, and the pigment is magnetic, it can be safely said that the pigment used is Canadian oxide, containing about 95 per cent of magnetic oxide. The so-called precipitated oxides of iron of the copperas varieties are extremely fine and of a rich cherry shade.

White Paints

It is well to study the characteristics of all the white pigments, for in those colleges where one or two samples of paint are given to the students in order to familiarize them with the analyses of paint, no attention is paid to the raw materials. As a general rule, sublimed white lead is regarded as sulphate of lead, but on glancing through the scant literature of paint chemistry it is found that the fault is not so much with the instructors as with those who have previously written on this subject. Many of the books describe sublimed lead or sublimed white lead as $PbSO_4$

and nothing else; whereas, the correct composition may be accepted as 70 per cent $PbSO_4$, 20 per cent PbO, and 5 per cent ZnO, and under all circumstances, even down to very small quantities, if these constituents are found in this ratio in a paint, sublimed white lead is indicated.

In the analysis of a mixed white paint a great deal of juggling is done with the carbonic acid which is liberated so that it is improperly distributed among the bases which are found. As an instance of this it can be cited that according to one rule all lead found is calculated to carbonate by multiplying by a factor, as for instance, 6.05. If there be any CO_2 left it belongs to the calcium present. This, then, having been disposed of, the SO_3 is given to the lime that is found. Then some manganese and lime will be found unsatisfied, and these, of course, are calculated as oxides or hydrated oxides.

A chemist having factory experience will at once see the incorrectness of an analysis of this kind, for the reason that no free alkali such as lime or magnesia can exist for any length of time in a mixed paint. If a manufacturer should add 4 or 5 per cent lime to his paint a saponification would take place which would ruin the whole mass and the paint would be unfit for use. It is, therefore, of some importance to the analyst to familiarize himself with the raw materials and their process of manufacture into a mixed paint so that the proper distribution of the acids be given, and if lead oxide is indicated and the paint be white, sublimed lead is positively present. Consequently all the CO_2 should not go to the lead but the sulphate should receive its proper place, and if a paint is of a uniform brush consistency no alkali can be reported. The absolute percentage of white lead in a paint (hydrated carbonate of lead) is very difficult

to establish, the ratio between the carbonate and hydrate in white lead varying quite largely.

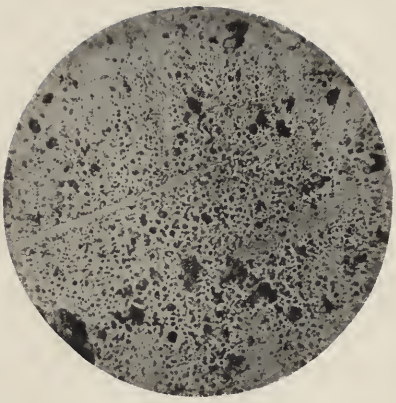
Sublimed white lead can generally be recognized by its ratio of oxide of lead to sulphate, but if a mixture were made of 70 per cent lead sulphate, 20 per cent lead oxide, and 5 per cent zinc oxide the chemist could not tell whether it was sublimed or not unless the paint under examination be a white paint, since the oxide of lead necessary for making this mixture would tint the white paint a straw color, whereas sublimed white lead is pure white. Twenty per cent of oxide of lead, either in the form of litharge or red lead, would saponify a paint, but sublimed white lead does not act in this manner. The method described under Sublimed White Lead, page 15, which is used in the laboratory of the author, can be followed out with accuracy.

Lithopone is easily distinguished by the liberation of sulphur as sulphureted hydrogen. There are only two other pigments which are likely to confound the chemist by giving this test. These are the sulphides of antimony and ultramarine. The former, however, is no longer used in mixed paints. In a white paint, of course, these pigments could not be used, for the antimony is orange and ultramarine is blue.

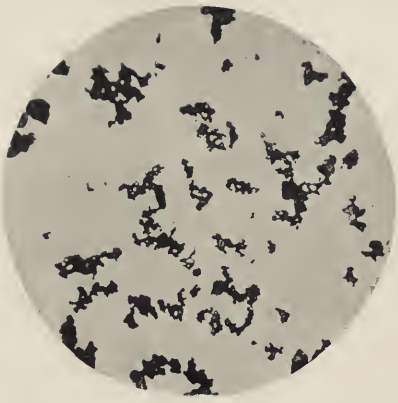
White and Light-Colored Pigments

The author refers the student to the excellent articles by G. W. Thompson on this subject in the J. S. C. I., June and November, 1896.

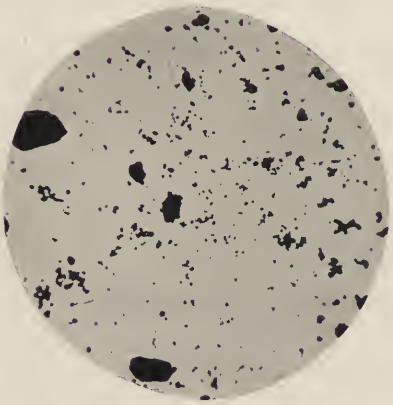
Arbitrary formulæ for many of the white pigments must be adopted for the purpose of obtaining concordant figures. white lead is usually stated to be $2PbCO_3$ and PbH_2O_2, but



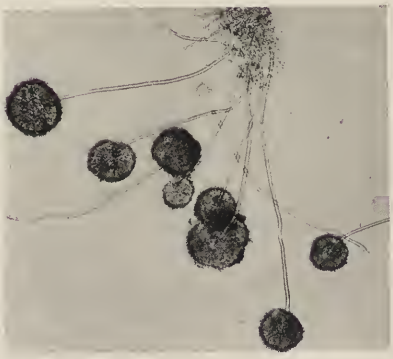
No. 47. Old Process White Lead — Photomicrograph X250.



No. 48. Natural Graphite — 90 per cent carbon, very finely powdered.



No. 49. American Hematite — Photomicrograph X250, showing a few large grains.



No. 50. Aspergillus Niger — Photomicrograph X100, black fungus frequently found on paint in cellars.

the proportion of hydrate and carbonate varies very largely and yet no definite notice can be taken of the variation.

Standard zinc lead white must be regarded as 50 per cent lead sulphate and 50 per cent zinc oxide although the constituents will vary very slightly from these figures. The variation in sublimed lead is not as great as the variation in corroded lead, for the obvious reason that sublimed lead is always made in the same way and of the same ore, whereas corroded lead is manufactured by different processes, causing differences in the percentage of hydrate. The new or quick process leads are for the purpose of simplicity classed under the head of corroded lead. If a white paint contains the relative percentage of lead oxide, lead sulphate, and zinc oxide characteristic of sublimed lead, even if these constituents are present in small amounts, sublimed lead must have been added, for the reason that no mixture of this kind can be made which will be white, and on the other hand we have the microscopic determination to aid us; the structure of sublimed lead being amorphous and the size of the grain remarkably uniform.

It is an easy matter to interpret the analysis of a paint which is composed of one or two white pigments, but it is not very easy and always uncertain when a mixture of pigments is used. If a straw-colored paint be composed of a white pigment and ochre the practical chemist can determine this better than the theoretical chemist. The tone and shade would indicate to the works chemist that the paint is largely composed of ochre, but the theoretical chemist will report a large percentage of clay and a small percentage of coloring matter. The two analyses will read so differently that by the one the paint would appear to be adulterated

and cheap, while by the other it would appear to be a pure high-grade paint.

The Analyses of Oils in Paint

The following is the method adopted by the author and given to his assistants:

"We determine the bromine number of oils by the method given by Parker C. McIlhiney in his pamphlet entitled "Report upon Linseed Oil and Its Adulterants." As given on page 9, it as is follows:

"About 200 milligrams of the oil are placed in a dry glass-coppered bottle and 10 c.c. of carbon tetrachloride run in from a pipette. Another pipetteful is run into another similar bottle. It is convenient but not absolutely necessary that both bottles should now be cooled by immersion in cracked ice. This causes the formation of a partial vacuum in the bottle. The bromine need not be allowed to react with the oil for more than a few minutes as the reaction is almost instantaneous. Twenty-five c.c. of a neutral 10 per cent solution of potassium iodide is introduced into each bottle by slipping a piece of rubber tubing of suitable size over the lip of the bottle, pouring the iodine solution into the well thus formed, and shifting the stopper slightly so as to allow the solution to be sucked into the bottle. If the bottle has not been cooled, cause the air as it escapes from the interior to be washed by bubbling through the potassium iodide solution. This method of introducing the iodide solution effectually prevents the loss of any bromine or hydrobromic acid. As soon as the iodide solution has been introduced, the bottle is shaken, and preferably set into the ice water for a couple of minutes or more so that there may

be no loss of drops of the solution when the stopper is opened, caused by a slight pressure inside of the bottle. The action between the bromine and iodide solution produces some heat and consequently pressure.

The free iodine is now titrated with neutral tenth-normal sodium thiosulphate, using as little starch as possible as indicator. At the end of this titration 5 c.c. of a neutral 2 per cent solution of potassium iodate is added. The hydrobromic acid produced by the action of the bromine on the oil liberates iodine from the potassium iodate and iodide. This iodine is now titrated with thiosulphate, a little more starch being added at the end of the titration. From the figures so obtained the total percentage of bromine which has disappeared is calculated. The percentage of bromine which has been converted into hydrobromic acid, called the "Bromine Substitution Number," is also calculated, while from these two the "Bromine Addition Number" is obtained by subtracting twice the Bromine Substitution Figure from the total Bromine Absorption. A consideration of the figures submitted will show that if an oil contains rosin, rosin oil, or mineral oil, the fact will be brought out by this process and an indication given by the figures so obtained as to which one is present. If the Bromine Substitution Figure is normal, the absence of more than a very small quantity of turpentine, benzine, rosin, or rosin oil is assured."

We follow this method closely, but take every possible precaution to exclude all trace of water until the addition of the potassium iodide solution. Traces of water influence the bromine number greatly. We also run a determination on linseed oil of known purity at the same time for comparison.

In presenting figures to the laboratory director, always

give the iodine number, which is obtained from the ratio of 80 to 127. There is no objection whatever in determining the iodine number by means of the Wijs, Hubl, or Hanus method, if you have the time.

Your report should also state whether the paint under examination dries over night or not, but inasmuch as darkness delays the drying action of linseed oil, you can for the first two hours of your examination spread a sample on glass and expose it to a dry heat of no higher temperature than 100° C. In the examination of raw linseed oil from carload shipments received at the works, compare with the known linseed oil adopted as the standard in the laboratory. It is very important that the temperature at which the oil breaks be reported, and any linseed oil which breaks below 450° F. should not be used but must be reported at once to the laboratory director. Linseed oil is apt to be cloudy when the temperature is below freezing. When a sample is brought into the laboratory it should be gently heated to 100° C. It will turn perfectly clear and brilliant. It should then be allowed to cool to the temperature of the room, and if it again turns cloudy it should be rejected and the varnish department notified not to use this oil for the manufacture of varnishes.

For making certain classes of paints, which are described in another schedule, this oil is perfectly good, provided it is placed in a refining tank. One half of 1 per cent sulphuric acid of the adopted strength should be slowly added in conjunction with a current of air. On the following day the requisite quantity of lime should be added to the oil, and at the end of two days the calcium sulphate, moisture, and "foots" which have settled out can be drawn off and set aside. The supernatant oil can then be

tested. It will then be found satisfactory and can be distributed.

Never condemn a carload linseed oil unless the chemical examination of each one of the laboratory assistants agrees. You need never look for adulterants in linseed oil, as the source from which it is purchased precludes the admixture of cottonseed oil, corn oil, or paraffin oil. You will find that the principal objection to linseed oil, if any, is in the percentage of "foots," and as all contracts are made for well-settled linseed oil the tests given heretofore are sufficient for decision.

The Microscope

Most students are, unfortunately, not sufficiently trained in the use of the microscope. Many hours of work are saved by those who know how to examine paints microscopically. The Nicol prism is likewise a valuable instrument and cases can be cited which will demonstrate this. Suppose a paint be sold under a guarantee that it is chemically pure and that zinc oxide is the only pigment. The chemist will examine it and find 1½ per cent silica, which he reports as an impurity. The matter is referred to another chemist who claims that the silica in the amount present is negligible and should not be taken note of, and that there is evidence to show that the paint was ground in a flint stone mill from which the silica in the paint was derived; no known method of manipulation can separate 1 per cent of silica from the finished paint. The silica shows up under polarized light as large arrow-shaped crystals polarizing in the various fields. This is absolute evidence of the fact that the silica in the paint is due to the attrition in the

mill. If silica were added as an adulterant it would not appear in the same field as zinc in polarized light, because the crystals would be entirely too small. Similarly, one chemist will often report that a paint is adulterated with barytes, and another chemist, who has sufficient knowledge and experience, will say the paint is not adulterated but contains precipitated barium sulphate, which in this case is a valuable constituent of the paint. Barytes is worth $20 per ton, and precipitated sulphate of barium from $60 to $80 per ton. Where it is possible to isolate the sulphate of barium, there are two excellent ways of determining whether it is precipitated or natural. The specific gravity of the natural is over 4; that of the artificial is under 2.6. This determination, however, is a long and tedious operation. The easier plan is to use the microscope, but familiarity with the amorphous appearance of the one and the crystalline appearance of the other is necessary before a decision can be rendered.

The question of the moral intent of the manufacturer must always be taken into consideration by the chemist.

The Spectroscope

In almost all of the factory laboratories, time is an important factor in an examination, and the chemist must learn to do quick as well as accurate work. Lime and barium compounds are largely used in the manufacture of mixed paints. The chemist who familiarizes himself with the "Spectra" of lime and barium can determine in less than a minute whether these elements are present or absent in a mixed paint.

The same is true in the examination of raw materials.

Although the spectroscope does not indicate quantity, if the barium lines flash up and disappear and the calcium lines persist, a subsequent analysis will show that there is a preponderance of lime over the barium salt. Students are taught to make a small loop of platinum wire about one eighth of an inch in diameter, fastened to a glass rod, and place some of the material on this loop and put it into the Bunsen flame. This is an expensive practice and cannot be recommended, since florists' iron wire or piano wire will serve the purpose just as well. When platinum wire is once used it is extremely difficult to clean it so that it shows no trace of a luminous flame, while the iron wire burns off clean in a few seconds.

A good way in which to prepare a mixed paint for the spectroscope is to burn off the vehicle and mix the ashes with nitric and hydrochloric acid so as to form a paste; place the eye to the telescope and observe the first flash. After a little practice the calcium and barium lines are easily recognized, and if, for instance, the violet potash line flashes up at the same time and the paint under examination is black or gray, the conclusion can be formed that one of the pigments in the paint is charcoal or vine black. Any lime in a paint must be determined quantitatively, for the reason that nearly all paints contain lime if the drier used is of the brown Japan variety, for the rosin in the brown Japan is generally neutralized with lime.

The Analysis of White Paints

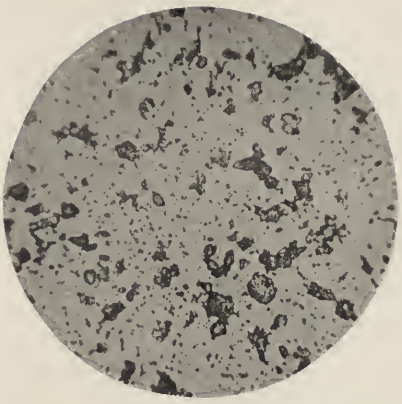
Method for determining Sublimed Lead in ready-mixed paints.

To extract oil, etc., a sample of the thoroughly mixed paint is placed in a tall beaker and stirred with ten volumes of benzine, heated on a sand or water bath and allowed to settle. The extract is decanted off and the operation repeated three times. After the last extraction, the pigment is poured on a filter paper and dried in an air bath at about 100° C.

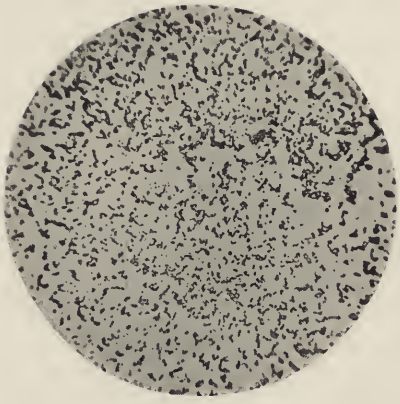
One gram of the dry pigment so obtained is weighed into a small beaker and digested with 50 c.c. of acetic acid (2 vol. of water to 1 vol. glacial acetic acid) on a sand bath for an hour or so, filtered and washed. This treatment removes zinc oxide, calcium carbonate, and oxide of lead from the oxysulphate of lead, leaving undissolved the $PbSo_4$. The filtrate is tested for zinc qualitatively, which is always present.

The residue and the filter paper are placed in the beaker in which the treatment with acetic acid was made, and to this is added 20 c.c. of water, 10 c.c. of strong ammonia (.90 sp. gr.), and a slight excess of hydrochloric acid. This is heated on a sand bath for several hours, filtered hot, and washed with hot water. The ammonium chloride dissolves the lead sulphate, leaving barytes, silicious matter, etc.

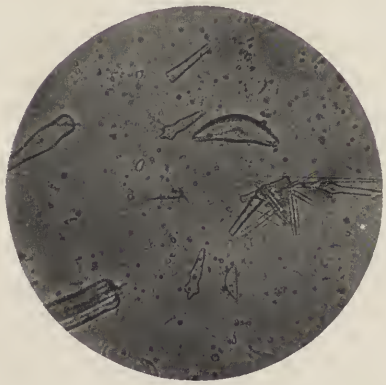
In this ammonium chloride extract, lead sulphate may be determined by two methods: first, from So_4; second, from Pb. First, by a gravimetric determination of So_4 as $BaSo_4$; second, by a determination of lead. For this purpose ammonium acetate is added to the ammonium chloride extract, whereby the solution is made acid with acetic acid,



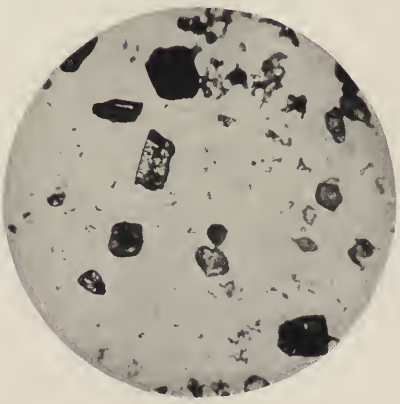
No. 51. American Barytes — Photomicrograph X250, sharp, angular, fairly uniform in grain.



No. 52. Lithopone (dry) — Photomicrograph X250, exceedingly fine and uniform in grain.



No. 53. Diatoms — Photomicrograph X500, found in whiting, clay, and infusorial earth.



No. 54. English Venetian Red — Photomicrograph X250, showing calcium sulphate crystals.

the lead precipitated by an excess of standard potassium bichromate solution, heated, allowed to settle, filtered and washed. To the filtrate is added potassium iodide and sulphuric acid, whereby the excess bichromate liberates iodine quantitatively.

After standing for about ten minutes the solution is made up to 250 to 300 c.c. and titrated with standard sodium thiosulphate solution with the addition of starch as indicator. The number of c.c. of standard potassium bichromate used to precipitate the lead as lead chromate is thus determined, and from this by calculation the amount of lead in the solution. From this data lead sulphate is calculated, and from this oxysulphate by dividing with the factor .75 (the average per cent of $PbSo_4$ in sublimed lead).

Zinc oxide is determined in the acetic acid extract of the pigments by the method of Galetti given on page 382 of Sutton's Volumetric Analysis. By this method the acetic acid solution of zinc, which must contain considerable ammonium acetate, is diluted to about 500 c.c., heated to 500 to 600 c.c. and titrated with standard ferrocyanide. The end point is found by the change of color from white to ash gray, which occurs when ferrocyanide is in excess. This may be confirmed by uranium acetate used as an outside indicator, which shows a faint brown on a white plate when ferrocyanide is in excess.

Zinc sulphide is determined in the same manner in the acid ammonium chloride extract after addition of ammonium acetate.

The Best Method for the Determination of Lead Sulphate is quoted from Professor J. C. Olsen's book on quantitative chemical analysis as follows:

Lead sulphate is quite insoluble in water, requiring

for its solution about 23,000 parts of cold water, but if the water contains sulphuric acid, 36,500 parts are required. The presence of alcohol reduces this solubility. Solutions of ammonium salts, especially the nitrate, tartrate, and acetrate, dissolve lead sulphate quite readily. The two latter should be rendered strongly alkaline with ammonia. It is also dissolved by the hot solutions of caustic soda or potash. Dilute nitric and hydrochloric acids dissolve considerable quantities of lead sulphate which is precipitated on the addition of dilute sulphuric acid. These acids are readily removed by evaporating the solution after the addition of sulphuric acid, until fumes of the latter appear. On diluting the solution with considerable water and adding alcohol, the lead is completely precipitated.

The lead precipitate should be washed by alcohol or dilute sulphuric acid, preferably by the former as the paper would char on drying if sulphuric acid were left in it, and if washed out by water some lead would be lost. On burning the paper some of the lead sulphate is reduced to metallic lead. The precipitate should therefore be removed from the paper, the latter placed in a porcelain crucible, and ignited until all carbon is burned. A drop or two of nitric acid and the same amount of sulphuric acid is added and evaporated off, care being taken to avoid spattering. The remainder of the precipitate should then be added and heated with a Bunsen burner. Sulphate of lead may very advantageously be filtered off on a Gooch crucible.

APPENDIX

THE CHINESE OIL TREE

Shanghai Report

The wood oil tree, or Aleurites Cordata, belongs to a family very common in China and known as the "tung." It is mentioned in one of the oldest books of the Chinese, where it is praised for its beautiful flowers and for the peculiar value of its wood in the manufacture of lutes. It is found growing in greater or less abundance * throughout the Yangtze Valley and to some extent in the south of China. According to Chinese classification, there are many varieties of the tree — the green tung, the white tung, the red tung, the wu tung, and the Ying tzu tung; but this classification is perhaps not accurate, for the Botanicon Sinicum places the wu tung in a different family. "It is the common Chinese name," we are told, "for the Sterculia platanifolia. The white tung, or, as it is also called, the pao tung, is classed as *Paulownia imperialis*, and is the variety from whose wood the lutes are made.†

The leaves, bark, and flowers of certain varieties are used in medicine. A bark of this name is exported in large quantities from Ningpo.

* The author is indebted to Mr. C. H. Kiessig for the Consular Report, translated by Mr. T. R. Jernigan. The original report was prepared by Interpreter E. T. Williams, who is also to be given credit.

† A fine specimen is growing in Central Park, N. Y., 59th Street side, near 6th Ave.

The wood oil tree is the ying tzu tung, so called from the shape of its fruit — ying meaning a jar. It is also known as the yiu tung or oil tung. It has been classed as Dryandra Corvata Thumb and as Eloeococco vernicia spreng or Aleurites Cordatavernicia montana lone.

Oil is also said to be derived from other varieties of the tung, but it is the ying tzu tung which is especially cultivated. for this purpose. It is found chiefly in Hunan, Hupeh, and Szechuen.

Hosie, in his "Three Years in Western China," says it grows in great abundance on the banks of the Yangtze west of Ichang, that it seems to prefer thin-soiled, rocky ground and grows to the height of 25 ft. It has large, beautiful, shady, green leaves, small pink-white flowers, and large green fruit like an apple. The seeds are large and poisonous, and it is from them that the oil is expressed. The fruit is gathered in August and September.

The machinery used for extracting the oil is very crude, consisting of wooden presses with wedges. It is sent to market in tubs of 80 catties (equals 107 pounds), with tight-fitting lids. The principal place of export is Hankow, whence in 1895 there were 290,631 piculs (38,741,112 pounds) shipped, chiefly to the Chinese ports, the value of which amounted to 1,453,156 taels ($1,162,524.80). Small quantities were exported from Kiukiang and Canton also. During the same year there was imported at Shanghai a quantity estimated at 90,385 piculs (12,048,320 pounds), valued at 488,078 taels ($390,462.40), of which more than 35,000 piculs (4,665,000 pounds) were re-exported.

The oil is used in the manufacture of paint and varnish, waterproof paper and umbrellas, and in western China it is used for lighting also. The greater part, however, is con-

sumed in calking, for which purpose it is everywhere used in China. In applying it to the bottom of the boats, it is put on hot, but for parts not commonly submerged it is put on cold and in thin coats. The upper part of a Chinese boat is oiled once or twice a month. This gives it a clear, glossy appearance and preserves the wood. According to the figures given above, the oil was worth 5 taels ($4.00) per picul at Hankow, and 5.40 taels ($4.32) at Shanghai. A picul is 133⅓ pounds, and this gives a little more than 3 cents (gold) per pound as the importing price in 1895. It sells at retail now (Feb. 1897) at from 120 to 160 cash (5 to 7 cents) per catty, according to quality.

It is said to be somewhat adulterated in the retail shops. Cheaper oils abound and the charge is not incredible. Cottonseed oil, it is reported, is used for this purpose.

Canton Report

In pursuance of instruction dated December 5, 1896, I have the honor to report a few facts collected in reference to the tung shu or Chinese oil tree, the Aleurites cordata.

By looking over the statistical tables for the different ports of China, contained in the Imperial Maritime Customs Gazette and Trade Returns for 1895 and 1896, we find that Canton is *not* the chief home of the tung shu which yields the tung yan, or wood oil, of Chinese commerce (packing for export done at Fatchau, below Canton and Hong Kong). On the contrary, we find that Hankow is the chief place of export, from which was exported to foreign countries and Chinese ports during the first three quarters of 1896, 188,556 piculs (1 picul equals 133⅓ pounds) of this native oil. But the likin office of Canton informs us that most of the wood oil that finds its way to Canton comes from Nganhwei Province.

Kweichow, in Kwangsi Province, is also said to make small shipments of this oil to Canton. I have it from reliable sources that the tree also grows at Lien-chau in Kwang-tung Province, near Hunan. It also grows in the islands of Formosa and Hainan, and is cultivated in Hong Kong.

Hankow being the principal place of export of the wood oil (but shows no import) it follows the oil must come to Hankow in junks or native boats down the Yangtze Kiang and other rivers. The most of this oil, as I am informed by reliable customs officers, comes from Szechuen Province, and the best of it is said to come from Hunan.

The above facts will serve to locate the tree, which may be said to grow in the provinces along the course of the Yangtze Kiang, but more abundantly on the south of it than on the north, except in Szechuen Province where it probably grows very extensively.

The tung shu attains to the height of from 10 to 20 or 25 feet, and grows on mountainous or hilly ground.

The oil is expressed from the nut or fruit of the tung shu by a process similar to that used for expressing the ground nut oil. The oil is usually of a light color, somewhat resembling linseed oil, and emits a nauseous odor.

It is extensively used for calking, painting, and varnishing, and preserving wood work generally. Almost all of the native boats on the Canton River are overdrawn with one or more coats of this oil, without the admixture of other ingredients and serving the same purpose that so many coats of paint do on other boats. The ink extensively used throughout the Chinese Empire is also made from the smoke of this oil.

As directly bearing on this subject I beg leave to quote

from Mr. Charles Ford, Superintendent of the Botanic Gardens, Hong Kong:

"Aleurites cordiata is a small tree which is cultivated in South China and as far north as the Yangtze Valley, as well as in Japan. The wood is said to be used for making lutes and is also excellent for making pillars for building purposes; it is also said to be never injured by insects. In South China I have seen it growing on hilly situations only when the soil was moderately good. The oil obtained from its seeds is used for painting all kinds of woods where exposed to moisture and also in the manufacture of oil paper. It is also, I understand, an ingredient in Chinese varnish, which is so extensively used for varnishing furniture. The oil is poisonous."

In bringing to a close my investigations in regard to the tung shu, permit me also to quote from the Chinese materia medica, which will illustrate the large sphere of usefulness occupied by the oil of this tree.

"The best wood oil comes to Hankow from Shin-chau Fu, in Hunan. The oil is given as a remedy in insanity and in cases of metallic poisoning. It is emetic, acro-narcotic, and drastic, proving destructive to rats in a very short time. It is applied as a stimulant to carbuncles, ulcers, burns, swellings, and bruises, and is a constant ingredient in native plasters. It was forbidden to be exported during the Taiping rebellion, as it is a necessary article for shipyards."

ALFRED ALF,
Vice-Consul in Charge.

CANTON, Feb. 10, 1897.

Hankow Report

In accordance with instruction, I have the honor to send full particulars in regard to the tung tzu shu (Aleurites cordata) or Chinese wood oil tree. It has taken me some time to obtain accurate information on the subject, in which I have been assisted by Rev. Joseph S. Adams and others. While large quantities of wood oil arrive here from up the river, it seems that but few persons know how it is extracted from the nut.

The tung shu, or wood-oil tree of China, is described as belonging to the Euphorbiacoe. Dr. Legge calls it Eloeococco dryandra. Dr. Wells Williams (Chinese dictionary, p. 934) describes it as Eloeococco ainensis. Dr. E. Bretschneider, in his Botanicon Sinicum, disagrees with Legge and Williams. Henry (p. 490) calls it the Paulownia imperialis; Bretschneider calls it the Dryandra cordata.

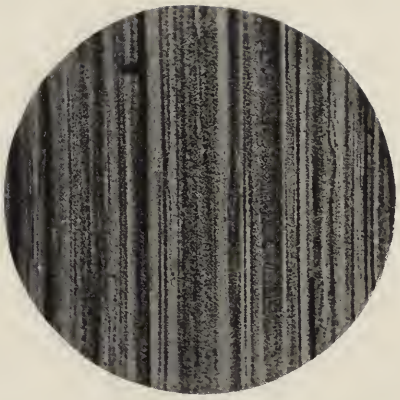
The tree is often referred to in Chinese classics. As early as the seventh century B.C., it is mentioned as being planted by Duke Wau around his house for its grateful shade, as it may be seen throughout China to-day.

There are many sorts of wood-oil trees: Hai tung (sea oil), a spinous variety, bark used for medicine; ts'ing tung, or green wood oil; pei tung, or white wood oil; chi lu tung, or red wood oil; wu tung, or patois name; yu tung or oil tree.

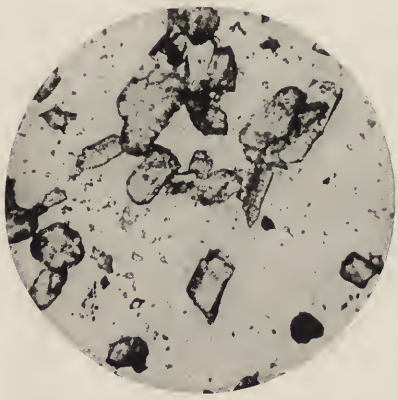
These colors refer to the flowers and not to any coloring quality in the oil. The oil is a clear or turbid, light or dark, thick fluid, depending for the shade on the kind of tree or the sort of treatment in manipulation. The pigment is added in painting or staining. The oil has no color save a faint, unbleached yellow when dry.

Description from Chinese sources. (See Bretschneider's

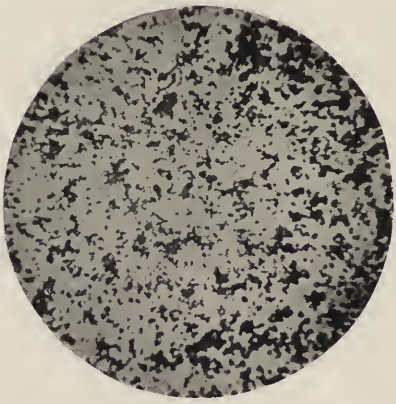
No. 55. ASPERGILLUS NIGER— Photomicrograph X100, old fungus found on paint.



No. 56. ULTRAMARINE BLUE, ground in oil, very uniform and fine, — Photomicrograph X250.



No. 57. AMERICAN GYPSUM — Photomicrograph X300, transparent flat crystals.



No. 58. ARTIFICIAL COBALT BLUE (same as Ultra Blue) — Photomicrograph X250, crystalline grain.

Botanicon Sinicum, p. 349.) It has very large leaves, variable in shape. The wood is light and *never injured by insects*. It is used for making various utensils and also excellent for making pillars in building houses. It flowers in March, its flowers are red, white, and purple in color. Its fruit is ripe in September and October. Its fruit is called by Chinese "Ying tzu tung," from its resemblance to a jar flattened at the top and bottom. It grows about as large as an orange. Within each capsule are five, and sometimes seven seeds. These are light, flattened, and winged like the seeds of an elm tree. When ripe the fruit bursts, and the seeds are carried off by the wind. It is a handsome tree, easily grown from seeds or cuttings, and attains a diameter of more than two feet. The trunk is very conical. It has cordate leaves and ovoid, acuminate fruit, withering and falling in the early frosts. It is not an evergreen. Its timber is praised for its quality in the manufacture of musical instruments, as the lute, etc. The older the tree and the higher it grows on a hillside the better its resonant timber. It is found along the Yangtze Valley from Szechuen to the sea, and especially in the provinces on both sides of the river. In the heart of China (Szechuen, Kweichow, Hunan, and Yunnan) the people spin thread from a tung tree and make a kind of cloth which resembles woolen. It is very common in Central China. It is also well known in Japan. There is a kind of bastard wood-oil tree from which strings can be made, probably Sterculia platanifolia (Henry).

The principal value is found in the oil produced from its large acrid and poisonous seed nut. This oil is largely used for painting and calking. *Mixed with sifted lime it makes excellent glacier's putty.* After the oil is removed, the nut is calcined or burnt and produces a very valuable soot,

from which Chinese ink is made (or India Ink, so called). *Cement, or chunam, for seams of boats, is made from this oil.* It costs about 90 cash (6 cents) per pint in the village where produced, and is sold at double that price in Hankow.

The nuts are gathered and dried, put in an ordinary Chinese rice "kwo," or cooking pot, — a shallow iron basin about 2 ft. in diameter, — and stirred about over a good fire until parched; they are then taken to a mill, sometimes worked by hand (an ordinary grinding mill) and ground to fine powder, the oil dripping out into a receptacle, or they are ground in a proper mill with large granite grindstones, turned by a cow, horse, or ass. When allowed to settle and strained through coarse grass cloth, the oil is ready for the market. *It is sent down in plaited baskets, lined with putty and varnished paper, with large wide mouths and four loops plaited in the bamboo to hook them up.*

The oil is extremely poisonous (when fresh). A simple native remedy (more effective, indeed, than any foreign one) is to boil a quantity of pine shavings in water and bathe the poisoned part repeatedly. It gives immediate relief and rapidly cures. The curious aspects of wood-oil poisoning are worthy of special study.

The wood-oil tree has been styled, and worthily so, the "national tree of China," from its stately appearance, green, smooth bark, and spreading branches.

There is no reason why this tree should not flourish in the United States and Europe, as it bears equally well at a temperature below freezing or up as high as 120° F., but the nut contains but little oil when grown outside of the provinces named. It could, no doubt, be grown profitably in our southern states or lower California.

This oil is used all over China as a paint or a varnish;

but little is exported. The nuts are gathered during the latter part of September and the early part of October, and the oil is brought by junks to Hankow during most of the year, and shipped to the various Chinese ports.

The customs returns show that, in 1894, 332,848 piculs (44,368,638 pounds) were exported from Hankow, and in 1895, 290,681 piculs (38,741,112 pounds). This does not include a large quantity used in Hankow, of which no return is made.

JACOB I. CHILD,
Consul.

HANKOW, Feb. 12, 1897.

CHUNGKING REPORT

Mr. Alexander Hosie, of the British Consular service in China, writing on the above-named tree in his work, "Three Years in Western China," says as follows:

"The oil tree (Aleurites cordata) was scattered about among the fields. It seems to prefer thin-soiled, rocky ground, being met with in great abundance on the banks of the Yangtze west of Ichang. It grows to the height of about 15 feet and has large, beautiful, and shady green leaves, which were lighted up as we passed with bunches of small, pink-white flowers. It produces a large green fruit like an apple, the large pips or seeds of which contain the oil for which the tree is famous. The fruit is gathered in August or September. Primitive wooden presses with wedges are used for extracting the oil, which is sent to market in wooden tubs with tight-fitting lids, and is employed for a variety of purposes, such as the manufacture of paint, varnish, waterproof paper, umbrellas, as well as for lighting. The seeds, if eaten, cause *nausea and vomiting.*"

The Journal of the China Branch Royal Asiatic Society has the following:

"The Dryandra, or Eleococco, to which Legge refers the tung of the classics, is indeed also a tung, but the Chinese authors distinguish it well from the Paulownia in terming it "ying tze tung" (ying is a jar, and allusion is made to the shape of the fruit); yu tung, oil-yielding tung."

Siebold says:

"This is the Dryandra cordata or Eloeococco verrueocc. A valuable oil pressed from the large, poisonous seeds is much used for painting and calking. The tree is extensively cultivated in the Yangtze Valley. It is also well known in Japan."

Archibald John Little, in his work "Through the Yangtze Gorges," has the following:

"The tung nut, which yields the oil, was being ground up in a circular stone trough by iron wheels, dragged around by a blindfold ox. The resultant coarse powder is then made into circular cakes with straw, and a horizontal pile is then placed in a very rough but solid wooden press, and long wedges are successively driven in and the oil expressed. These wedges are iron capped and are struck by a huge ram slung from the roof and worked by two men, the taking-count rim being an affair of much nicety. The oil cake remaining is a valuable manure for the poppy. Opium and tung (Eloeococco, or varnish tree) oil are the two main staples of eastern Szechuen."

From a native source (my own writer) I have obtained the following:

"The names of the tung shu are numerous. In the Chinese classics, the diameter of the tree is referred to be

just an armful, and it is also mentioned in the Book of Poetry. In other books it is stated that the wood was used for making harps, and the leaves were able to tell when it was an intercalary month by shedding an extra leaf; the flower also knows when it is cold. But it is not stated in books what the fruit was used for. It grows to the height of about 20 feet and the shortest is about 8 or 9 feet high. When the flower is red it is called the red tung shu, and when the flower is white it is called the white tung shu, and further there are the kau tung and tze tung. In the Chuen-fong-pu, the white tung shu is also called the hwa tung, pau tung, in tzu tung and hu tzu tung. The kau tung is just the same as what they now call the yu tung and the fruit is like the poppy. The outside of the flower is white and the inside is red. During the latter part of the second moon and the beginning of the third moon it commences to flower; in the fourth or fifth moons it becomes a fruit, which does not ripen until the end of the eighth moon, when it is beaten from the tree with bamboos and put in damp places until the outside gets rotten, and then the kernel is taken out. The size of the kernel is about the size of a bean. When the outside is peeled off, it becomes pure white. It is roasted until burnt and then ground; then they put it into a bowl and steam it, when cakes are made from it. It is afterwards put into a press and the oil obtained, which is used for lamps and also to give polish to painted things."

As will be seen from the foregoing information, the fruit does not ripen until the end of the eighth moon — about the first of August. I have, therefore, been unable to visit one of the places where the manufacture of the oil takes place and report in full on the process and the quantity produced.

I hope next autumn to be able to furnish an additional report on the subject. GEO. F. SMITHERS,

CHUNGKING, April 14, 1897. *Consul.*

CHINESE OIL TREE SUPPLEMENTARY REPORT

The t'ung-tsz, or wu tung, is usually described as the Eleococca vernicia, or verrucosa, but according to the highest botanical authority is more correctly termed Aleurites vernica. This tree flowers in the month of March or April and produces the fruit a month later. It is plucked about September or October and allowed to rot in heaps covered over with grass in order that the kernel may be disengaged from the shell or husk. The t'ung shu grows in hilly places all over the province of Szechuen, but half of the whole production is stated to come from the eastern portion, three tenths coming from the southern districts and one tenth from each of the western and northern parts. Of the produce of the eastern portion, one fifth comes from Fuchau, Peng-shin and the Kung-t'an River; one fifth from K'i Kiang, and the border of Kwei Chow Province; one fifth from Liang-Shan, Tien-Kiang, Wan Hien, and Chung Chow, and the remainder from the other districts. The nuts are divided into three different varieties — the yellow, drab (ma, or hemp colored), and white, the last affording the greatest quantity of oil.

There is no market for the nuts at Chungking, the crushing being invariably done locally, nor is there any tax upon them *in transitu.* The husks, and in places where there is no crushing industry the nuts themselves, are burnt for potash, the other sorts of potash in use being obtained from pulse and from grass, the best grass being the ma-pien ts' ao (Verbena Officinalis). The cake, after the extraction

of the oil, is used extensively as manure for tobacco, as are also the husks where not utilized for obtaining potash.

The oil manufacture of Szechuen is not so extensive as that of T'ung-Jen tu in Kwei Chow Province; but still it is very considerable, the neighborhood of Fuchau monopolizing the greater part, Wan Hien and Chung Chow coming next.

The value of the oil at the place of manufacture is usually about 45,000 cash the ordinary picul (about $3.00 gold per 133⅓ pounds).

The cake manure is chiefly esteemed in the cultivation of the best tobaccos in the northern parts of Szechuen. It is sold by the trade scale of 105 catties to the picul at the rate of about 5 mace, or 700 cash (about 46 cents). There are two varieties, known as the autumn (ch'in) and fire (hwo) cake, the latter containing less oil and being a trifle cheaper than the former.

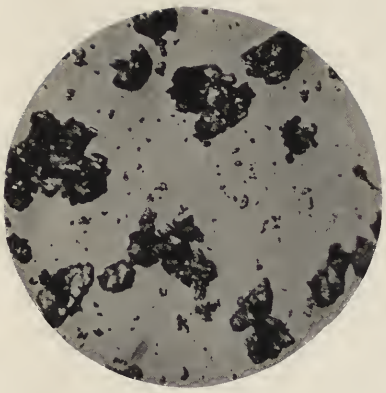
The chief export of oil to Hankow seems to be from T'ung-Jen in Kwei Chow by way of Ch'ang-te and is mostly in the hands of Kiang Si men. The country people take it to the T'ung-Jen market in loads of two wicker baskets, each basketful weighing 80 catties (106 pounds).

The chief uses of the t'ung oil are to varnish boats, feed lamps, varnish houses and furniture, make umbrellas and waterproof cloth, and manufacture the best ink. This is done by obtaining the soot resulting from the combustion of lampwick grass (Cyperus difformis) (Cinn) and T'ung oil in a small furnace. Of late years it has also been used for building forts, forming with tripartite earth (sau-ho-tu) of lime, sand, oil, and clay, *a material almost as tough as granite.* In the district of Nau Ch'uan there are said to be two sub-species, one a small tree, the fruit of which has only two figs. The other kinds have four, six, and eight

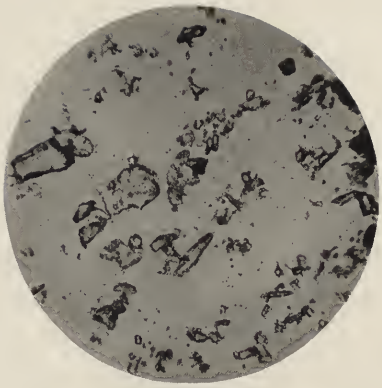
"figs," or lobes, each containing two kernels. The nuts are also distinguished into the round and flat. The flower of the white nut is white, that of the yellow nut red, and that of the mouse-colored (ma) speckled (tsa).

The crushing of the t'ung oil is done in the following way:

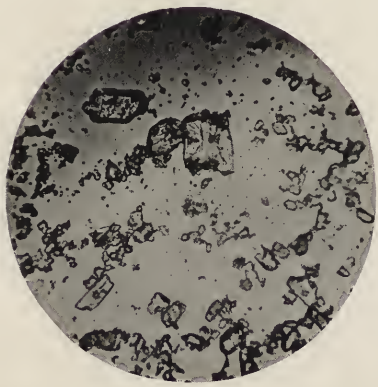
The kernels, having been removed from the husks, are first ground in a stone mill, and then steamed in a wooden tub until they become soft. They are in this condition placed within 24 iron hoops about 18 inches in diameter and half an inch in thickness, and separated from each other by about one inch, the whole resembling a huge screw or sausage. This is then placed horizontally in a sort of hollow horse, or strong wooden frame, and an arrangement of wooden blocks and wedges is laid across one end of the sausage, the other resting against the inner end of the horse. Two of the wedges are very much longer and stronger than the other blocks, and are strongly capped with iron at the ends facing the operator. One, thick at the inner and very thin at the outer end, is driven in so as to compress the cake; whilst the other, thick at the outer and thinner at the capped end, is used to release the cake when ready. A battering-ram, strongly capped with iron, swings from a beam of the building, running at right angles to the direction of the ram and parallel to the direction of the horse with its sausage-like contents. A man swings the ram twice or thrice backward and forward, and finally brings down its heavy cap with great force on the iron head of the wedge, which, advancing of course, tightens the blocks and squeezes the pulpy mass. The oil drops down into sort of a gutter running around a basin or cistern and is conveyed away by bamboos to other receptacles. Twelve cakes, each about $1\frac{1}{2}$ inches in thickness and weighing each about 14 catties



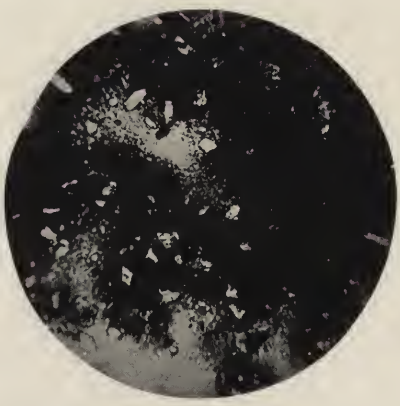
No. 59. French Terra Alba.— Photomicrograph X250, composition $CaSO_4 + 2H_2O$ same as gypsum. Brilliant white due to its coarseness.



No. 60. Asbestine — Photomicrograph X250, similar in size and shape to fine American gypsum. Used to prevent white paints from settling. Composition Silicate of magnesium. It is entirely inert.



No. 61. American Gypsum — Photomicrograph X250, fairly uniform and flat crystals.



No. 62. American Venetian Red — Photomicrograph X250, showing fine grains of Calcium Sulphate.

(18 pounds) are taken from the 24 iron hoops. Before being used as manure, these cakes are once more triturated. The local retail trade in the t'ung oil is conducted at the rate of 20 ounces to the pound.

The above is from a work by Mr. E. H. Parker, entitled "Up the Yangtze," published in 1891.

GEO. F. SMITHERS,
Consul.

CHUNGKING, Oct. 22, 1897.

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